

Effects of interfacial adhesion on the rubber toughening of poly(vinyl chloride)

Part 2. Low-speed tensile tests

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Abstract

The influence of interfacial adhesion on the tensile properties, including toughness, of poly(vinyl chloride) (PVC)–nitrile rubber (NBR) blends with the morphology of well-dispersed rubber particles has been investigated using two types of blends. The first type, which contains NBR26 (NBR with 26 wt% acrylonitrile (AN)), has a higher interfacial adhesion strength than the second type that contains NBR18. The secant modulus and yield stress of the blends were found to be independent of interfacial adhesion. On the other hand, the elongation-at-break and toughness (defined as the area under the stress–strain curve to break) depend strongly on the interfacial strength. The effects of rubber particle size, size distribution and rubber volume fraction on the tensile properties have been combined into the effect of a single morphological parameter, the matrix ligament thickness T . Both the elongation-at-break and toughness increase as T decreases. At $T < 0.06 \mu\text{m}$ the blends with stronger interfacial adhesion (PVC–NBR26) have much higher elongation-at-break and toughness. Stress whitening was observed in all deformed PVC–NBR18 blends. For PVC–NBR26 blends, however, stress whitening occurred only at $T > 0.06 \mu\text{m}$. Transmission electron microscopy studies revealed that debonding at the PVC–NBR interface is the sole microvoiding mechanism that causes stress whitening. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The toughness of a plastic can be enhanced substantially by blending with rubber particles [1]. Both morphological parameters and interfacial adhesion between the matrix and the dispersed particles play important roles in controlling the toughness of the blends. It is commonly believed that the effects of morphological parameters and interfacial adhesion are interrelated. For instance, strengthening the interfacial adhesion leads to a better dispersion of particles and smaller particle size and hence a change of toughness. This effect of interfacial adhesion on toughening is termed indirect [2]. On the other hand, interfacial adhesion may have a direct effect on toughening when the morphological parameters are identical [2].

At constant interfacial adhesion, the toughness of plastic–rubber blends measured at low speeds of deformation is a function of morphological parameters, i.e. rubber particle

size, volume fraction and particle spatial distribution parameter. Muratoglu and coworkers [3] demonstrated that there is a substantial influence of both rubber particle size and volume fraction on the elongation-at-break and toughness of nylon 6–rubber blends. The toughness (defined as the area under the stress–strain curve to break) was found to increase with increasing rubber content for a constant rubber particle size and with decreasing rubber particle size for a constant rubber content. Takaki and coworkers [4] reported that the effects of both the size and volume fraction of methyl methacrylate–butadiene–styrene graft copolymer (MBS) particles on the elongation-at-break and the toughness of poly(vinyl chloride) (PVC)–MBS blends can be combined into the effect of a single parameter, namely the matrix ligament thickness. These properties were found to increase with decreasing matrix ligament thickness. Kim and coworkers [5] reported that the rubber particle spatial distribution has a substantial influence on the elongation-at-break values of styrene–acrylonitrile copolymer (SAN)–rubber blends.

However, interfacial adhesion has been reported to have little direct effect on the toughness of the polymer–rubber

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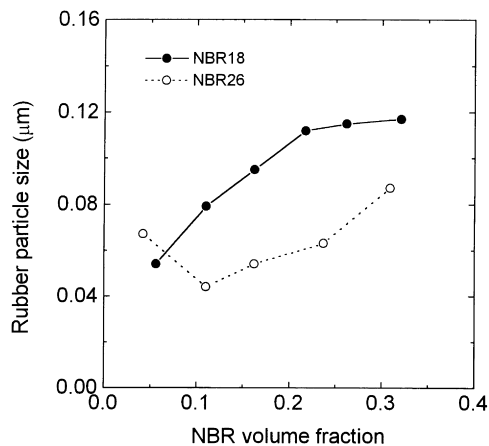


Fig. 1. NBR Rubber particle size versus NBR volume fraction for PVC-NBR18 and PVC-NBR26 blends.

blends at low strain rates. Dompas and coworkers [6] investigated the effect of interfacial adhesion on the stress-strain curves of the PVC-MBS blends by using a constant volume fraction of MBS particles of size of 0.25 μm . They concluded that the interfacial adhesion has no influence on the stress-strain behavior of the blends. Huang and coworkers [7] found that interfacial adhesion has only a small effect on the fracture behavior of rubber-toughened epoxies. Cho and coworkers [8] investigated the effect of interfacial adhesion on the fracture toughness of the poly(methyl methacrylate) (PMMA)-rubber blends determined by three point-bending tests. By studying the fracture toughness as a function of the rubber particle size at a constant rubber content, they concluded that interfacial adhesion does not have any influence.

The interfacial adhesion between PVC and nitrile rubber (NBR) can be strengthened through an increase of the acrylonitrile (AN) level in NBR in the range of 0–40% by weight [9]. Imasawa and Matsuo [10] studied the strain rate dependence of the elongation-at-break for PVC-NBR blends with various AN contents. The NBR phase as well as the PVC phase in these blends were continuous [9]. However, it was not possible to separate the effects of morphological parameters and interfacial adhesion for blends with co-continuous phases due to lack of a theoretical framework.

In the first paper of this series, we reported the direct influence of interfacial adhesion on the impact strength of PVC-NBR blends with the morphology of well-dispersed rubber particles [2]. In the present work, we use the same PVC-NBR blends with two different levels of interfacial adhesion to investigate the direct effect of interfacial adhesion on the toughness of the blends determined by the low-speed tensile measurements. Microvoiding mechanisms, such as crazing [1], internal cavitation of rubber particles [6,11] and debonding between the matrix and dispersed particles [2,12–14], relieve the triaxial dilatational stresses ahead a crack tip, thereby promoting plastic

deformation. Therefore, microvoiding is one of the most important toughening mechanisms. In this paper, the role of microvoiding in the toughening of the PVC-NBR blends is also discussed.

2. Experimental

2.1. Materials and blend preparation

The raw materials used and the PVC-NBR18 and PVC-NBR26 blends were described in previous papers [2,15].

2.2. Measurements of tensile mechanical properties

Tensile tests were performed according to ASTM standard D638M on an Instron 8511 machine at a crosshead speed of 100 mm min^{-1} and at a temperature of 25°C. The secant modulus at a strain of 0.02 was computed. The yield stress and elongation-at-break were also measured. The toughness was taken as the area under the stress-strain curve calculated with the aid of a computer.

2.3. Examinations of deformation mechanisms

Sectioning was performed under cryogenic conditions (-100°C) using a microtome equipped with a glass knife. Ultrathin sections were stained using osmium tetroxide (OsO_4) vapor so that the NBR phase appears to be dark in the transmission electron microscope (TEM) pictures. The damaged zones of the PVC-NBR blends were observed on a Hitachi H-800 TEM.

A small piece of a PVC-NBR26 blend was cut from a tensile bar after being subjected to a tensile test. The small sample was immersed in liquid nitrogen and then fractured. The cryo-fractured surface was coated with gold, and was then observed on a Leica Stereoscan 440 scanning electron microscope (SEM).

3. Results and discussion

3.1. Morphology

All the PVC-NBR blends investigated have identical dispersion states of rubber particles, i.e. the morphology of well-dispersed particles shown in our previous papers [2,15]. The sizes of the rubber particles in the blends follow the log-normal distribution. The average rubber particle sizes at the probability of 50% in log-normal plots are depicted in Fig. 1. The rubber particle size in the PVC-NBR blends increases generally with rubber volume fraction. At any given rubber volume fraction, the rubber particle size in a PVC-NBR26 blend is smaller than that in a PVC-NBR18 blend. The difference in particle size is quite great when the rubber volume fraction is between 0.1 and 0.3.

The AN content (26 wt%) in NBR26 is higher than that

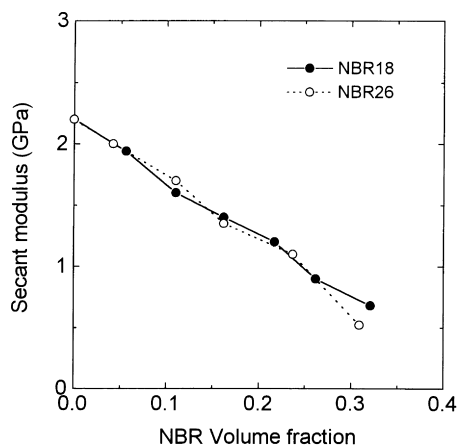


Fig. 2. Secant modulus versus NBR volume fraction for PVC–NBR18 and PVC–NBR26 blends.

(18 wt%) in NBR18. The interfacial adhesion between the PVC and NBR26 is thus stronger than that between the PVC and NBR18, and this leads to finer rubber particle sizes when the processing conditions are identical. It should be noted that the two blends with rubber volume fractions of 0.042 and 0.056 were prepared at lower shear stresses and shorter mixing times compared to the other blends.

3.2. Mechanical properties

The tensile properties of the PVC–NBR blends with the two different levels of interfacial adhesion were measured at a crosshead speed of 100 mm min^{-1} . Fig. 2 shows the variation of the secant modulus (at a strain of 0.02) with rubber volume fraction. The secant modulus decreases monotonically with increasing rubber content, and is independent of interfacial adhesion. As shown in Fig. 3, the yield stress is also not affected by interfacial adhesion, and depends on the rubber content in a manner similar to the secant modulus. We have reported that the glass transition temperatures for the two rubbers are identical, $-50 \pm 1\text{C}^\circ$ [2]. Therefore, the

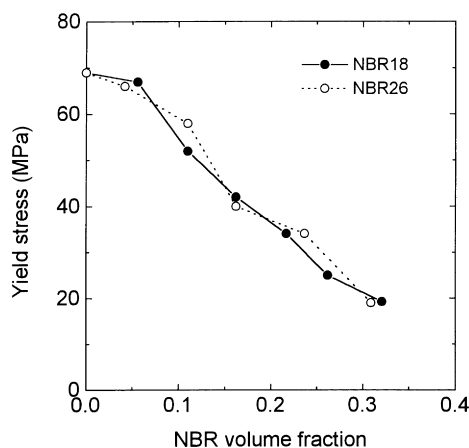


Fig. 3. Yield stress versus NBR volume fraction for PVC–NBR18 and PVC–NBR26 blends.

mechanical properties, i.e. modulus and yield stress, of the two rubbers should be similar at room temperatures. Accordingly, the modulus and yield stress of the two blends are also similar.

The elongation-at-break of the blends increases with the rubber content (Fig. 4). The elongation-at-break values for the PVC–NBR18 and PVC–NBR26 differ very little when the rubber volume fraction ϕ is lower than 0.125. At higher ϕ , the elongation-at-break of the PVC–NBR18 blends has a stronger ϕ dependence, so it has increasingly higher value than that of the PVC–NBR18 as ϕ increases. As shown in Fig. 5, the toughness has a similar ϕ dependence as the elongation-at-break. For a given ϕ , the toughness of PVC–NBR blends is determined mainly by the elongation-at-break and accordingly by the interfacial adhesion between PVC and NBR.

In general, both the modulus and yield stress of a plastic–rubber blend depend mainly on the rubber volume fraction rather than on the rubber particle size or size distribution. However, both the elongation-at-break and toughness were shown to be a function of the rubber volume fraction and rubber particle size [3–5]. The effects of these parameters on the elongation-at-break and toughness may be combined into the effect of a single parameter, the matrix ligament thickness. Recently Takaki and coworkers [4] reported that the toughness of the PVC–MBS blends measured at a low tensile speed of 9.6 mm min^{-1} is a function of the MBS particle size, MBS content and matrix ligament thickness. They obtained a master curve by plotting toughness against the matrix ligament thickness for three MBS particle sizes of 0.084, 0.169 and $0.235 \mu\text{m}$. They also presented a master curve of elongation-at-break against matrix ligament thickness. Gloaguen and coworkers [16] also emphasized the importance of matrix ligament thickness in rubber toughened PMMA at low strain rates.

We have plotted the elongation-at-break and toughness against matrix ligament thickness (surface-to-surface interparticle distance) for the two PVC–NBR blend systems (Figs. 6 and 7). The matrix ligament thickness (T) was calculated from [17–19].

$$T(d, \sigma, \phi) = d \left[\left(\frac{\pi}{6\phi} \right)^{1/3} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma) \right] \quad (1)$$

where d is the rubber particle size at the probability of 50% in a log-normal plot, ϕ the rubber volume fraction and σ is the particle size distribution parameter.

Fig. 6 shows that the elongation-at-break for the PVC–NBR blends increases with decreasing T . At $T > 0.1 \mu\text{m}$ the PVC–NBR18 and PVC–NBR26 blends have similar elongation-at-break. Below $T = 0.1 \mu\text{m}$ the elongation-at-break for the PVC–NBR18 blends rises to values that are significantly higher than those for the PVC–NBR26 blends. However, at $T = 0.06 \mu\text{m}$, there is a sharp increase in the elongation-at-break for the PVC–NBR26 blends such that,

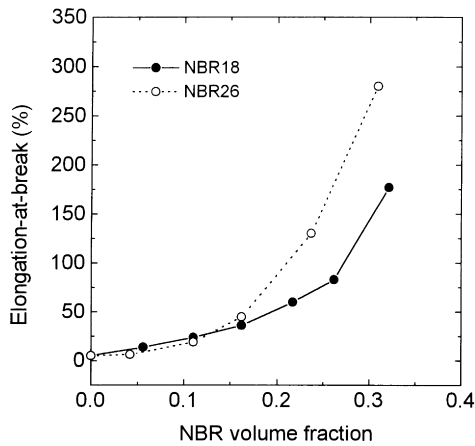


Fig. 4. Elongation-at-break versus NBR volume fraction for PVC–NBR18 and PVC–NBR26 blends.

at $T < 0.06 \mu\text{m}$, this type of blends has a substantially higher elongation-at-break than the PVC–NBR18 blends. As shown in Fig. 7, the toughness of the PVC–NBR blends exhibit the same dependence on T as the elongation-at-break.

3.3. Deformation mechanisms

It was found that the degree of whiteness in the stress-whitened region of the tested bars decreases with increasing ϕ or decreasing T . Stress whitening was observed in all of the PVC–NBR18 samples studied. Stress whitening was also observed in a PVC–NBR26 sample with $T = 0.3 \mu\text{m}$. However, the PVC/NBR26 samples with $T < 0.06 \mu\text{m}$ did not show any stress whitening.

Stress whitening may result from crazing in the matrix, internal cavitation of the rubber particles or debonding at the matrix–particle interface. All these microvoiding mechanisms can be examined by TEM. The TEM micrograph of an undeformed PVC–NBR18 blend did not show any void [2]. So, the voids observed in the following TEM micrographs

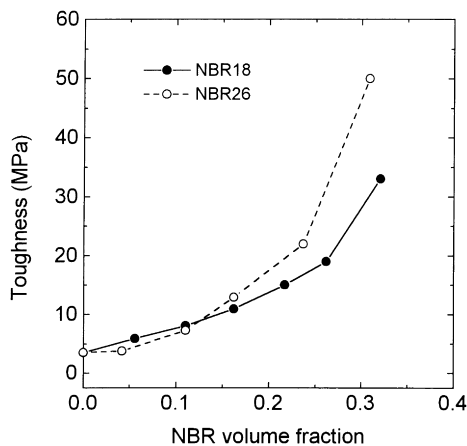


Fig. 5. Toughness versus NBR volume fraction for PVC–NBR18 and PVC–NBR26 blends.

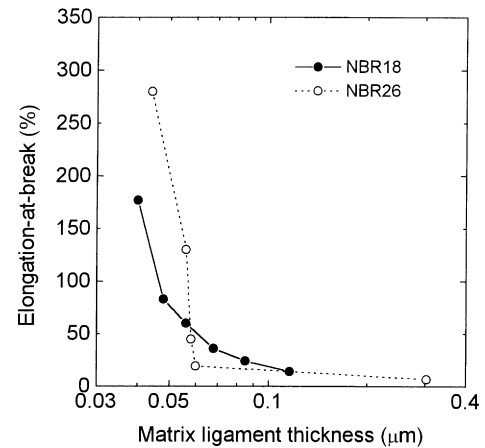


Fig. 6. Elongation-at-break versus matrix ligament thickness for PVC–NBR18 and PVC–NBR26 blends.

arise from microvoiding in the PVC–NBR blends caused by the tensile deformation process.

Fig. 8 shows the TEM micrograph of an intensively stress-whitened region of a deformed PVC–NBR18 blend with $T = 0.116 \mu\text{m}$. There are basically three levels of grayness in Fig. 8: (1) the dark dots represent rubber particles stained by OsO_4 ; (2) the light gray regions denote the PVC matrix; and (3) the white dots denote voids. It is obvious that the voids are formed because of debonding at the PVC–NBR18 interface. For a PVC–NBR18 blend with $T = 0.04 \mu\text{m}$ stress whitening was not intense and was observed only near the sample surface. Only a small number of voids are seen in the TEM picture (Fig. 9), and the voids are formed as a result of interfacial debonding. Therefore, the PVC–NBR18 interface is not strong enough to resist debonding. It is also seen that rubber particles are highly elongated in the above two samples.

Fig. 10 shows that for a PVC–NBR26 blend with $T = 0.3 \mu\text{m}$ voids are formed due to debonding at the PVC–NBR26 interface. Like the PVC–NBR18 blends, the

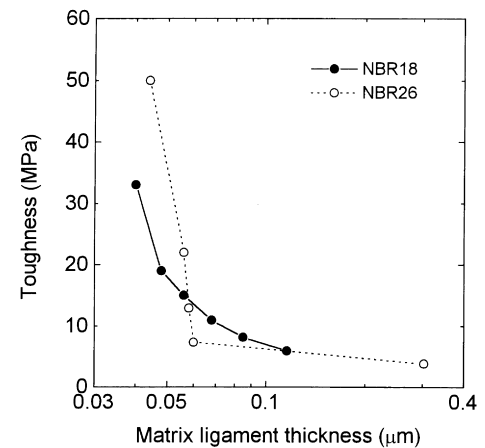


Fig. 7. Toughness versus matrix ligament thickness for PVC–NBR18 and PVC–NBR26 blends.

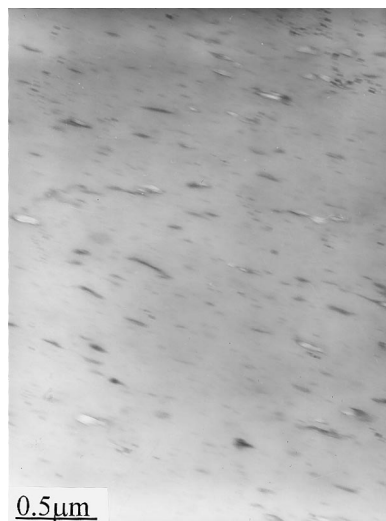


Fig. 8. TEM micrograph for a PVC–NBR18 blend with $T = 0.116\mu\text{m}$ taken in the stress-whitened region, showing debonding at the PVC–NBR18 interface.

strength at the interface of the PVC–NBR26 blends is not high enough to resist debonding.

SEM was also used to search for voids in the PVC–NBR26 blends ($T < 0.06\mu\text{m}$) which did not exhibit stress whitening. The cryo-fractured surfaces that were observed by SEM are denoted as “SEM observation surfaces” in the upper part of Fig. 11. For a PVC–NBR26 blend with toughness of 50M Pa and $T = 0.044\mu\text{m}$, no voids can be seen on the cryo-fractured surface (Fig. 11). Therefore, for PVC–NBR26 blends with $T < 0.06\mu\text{m}$, neither debonding nor internal cavitation of rubber particles was induced by the deformation process.

For $T > 0.06\mu\text{m}$ the elongation-at-break and toughness of a PVC–NBR18 blend are higher than those of a PVC–

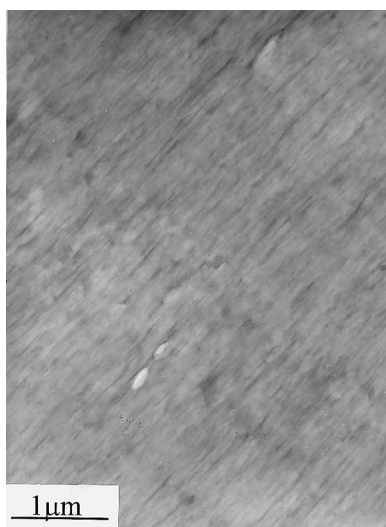


Fig. 9. TEM micrograph for a PVC–NBR18 blend with $T = 0.04\mu\text{m}$ taken in the stress-whitened region, showing debonding at the PVC–NBR18 interface.

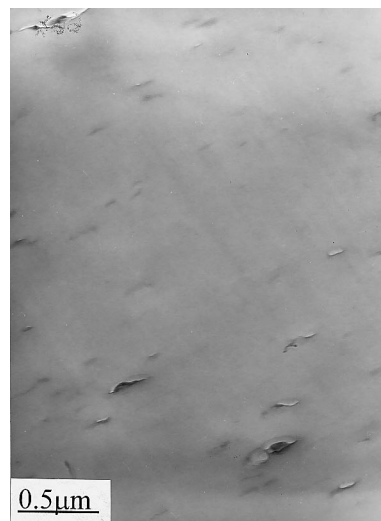


Fig. 10. TEM micrograph for a PVC–NBR26 blend with $T = 0.3\mu\text{m}$ taken in the stress-whitened region, showing debonding at the PVC–NBR26 interface.

NBR26 blend, indicating that debonding relieves triaxial tension, thereby promotes shear yielding in the PVC–NBR18 blends. At lower T the elongation-at-break and toughness of the PVC–NBR26 blends are, however, greater than those of the PVC–NBR18 blends. This suggests that for $T < 0.06\mu\text{m}$ shear yielding of the PVC matrix can occur readily in the PVC–NBR26 blends without interfacial debonding. In this case debonding is no longer a dominant mechanism for relieving triaxial tension and promoting shear yielding.

There is a great difference between the direct effect of interfacial adhesion on toughening observed in this work

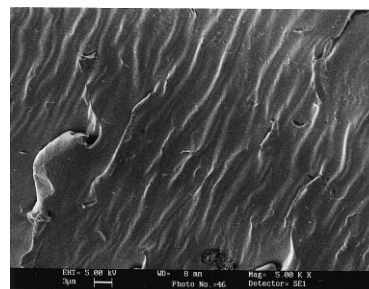
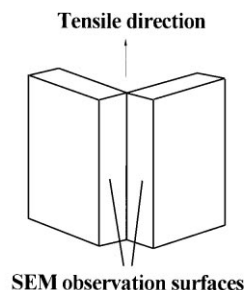


Fig. 11. SEM micrograph for a PVC–NBR26 blend with $T = 0.044\mu\text{m}$ taken in the deformation region. The location of observation surface is indicated in the upper part of this figure.

and that reported in the first paper in this series. In our previous work debonding between the PVC and NBR phases is the dominant microvoiding mechanism for achieving high impact strength in PVC–NBR blends [2]. However, in this study, it is seen that debonding leads to a lower tensile toughness in the PVC–NBR blends at $T < 0.06 \mu\text{m}$. It is thus clear that the conclusions on the effects of interfacial adhesion in toughening derived from the low-speed tensile tests cannot be applied readily to impact measurements. Therefore, care must be taken when one uses the knowledge obtained at low strain rates and in one deformation mode to explain the data measured at high strain rates and in another deformation mode.

4. Conclusions

Using NBR rubber containing 18 and 26 wt% acrylonitrile we have prepared two types of blends, PVC–NBR18 and PVC–NBR26, with the PVC–NBR26 blends having stronger interfacial adhesion. This allows an investigation of the effect of interfacial adhesion on the tensile properties of the PVC–NBR blends with the morphology of well-dispersed NBR rubber particles.

At a low tensile speed of 100 mm min^{-1} , the secant modulus and yield stress of the blends are independent of interfacial adhesion. On the other hand, the elongation-at-break and toughness depend strongly on interfacial strength. The effects of rubber particle size, size distribution and rubber volume fraction on tensile properties have been combined into the effect of a single morphological parameter, the matrix ligament thickness T . Both the elongation-at-break and toughness increase as T decreases. At $T < 0.06 \mu\text{m}$, the PVC–NBR26 blends with stronger interfacial adhesion have much higher elongation-at-break and toughness. At high T , however, the PVC–NBR18 blends with weaker interfacial adhesion have slightly higher elongation-at-break and toughness.

Stress whitening was observed in all PVC–NBR18 blends after tensile deformation. However, for the PVC–NBR26 blends, stress whitening occurred only at $T > 0.06 \mu\text{m}$. The intensity of the stress whitening weakens as

T decreases. TEM studies revealed that debonding at the PVC–NBR interface is the sole microvoiding mechanism that causes stress whitening.

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