

Nitrile Glove Waste as Blending Component for Natural Rubber and Epoxidized Natural Rubber: Functionality and Thermal Stability

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Blends of Natural Rubber/Recycled Nitrile Rubber (NR/r-NBR) and Epoxidized Natural Rubber/Recycled Nitrile Rubber (ENR/r-NBR) were prepared on a two-roll mill. Thermal studies, namely thermo-oxidative ageing and thermogravimetric analysis (TGA), were carried out for comparison. Thermal ageing and TGA of the blends containing a high weight ratio of r-NBR suggested higher thermal stability, as they showed increased tensile properties and elongation at break as well as initiation of degradation at higher temperatures. This is because r-NBR consists of a crosslinking precursor and has greater thermal resistance. At similar blend ratios, it was observed that using ENR instead of NR as a blending component resulted in higher thermal stability. This is likely due to the higher thermal stability of ENR. Replacing epoxy rings on the rubber backbones gives ENR improved resistance to heat ageing. The results of thermal ageing tests agreed with the TG profiles of the blends, where higher values for tensile retention and elongation at break correlated with higher decomposition temperatures.

Keywords: Nitrile Rubber; natural rubber; epoxidized natural rubber; recycling; blends

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The demand for medical and surgical gloves increased significantly with the declaration of the COVID-19 pandemic in March 2020, as demand from traditional users in the medical profession grew while others began using medical gloves in their daily activities, including front-line workers, transportation workers, and even the general public. Increased global production could only accommodate a portion of the increase in demand [1, 2]. As a result, the global glove shortage persists and is expected to continue into 2022. There are four main types of gloves that are used in a medical and surgical context, namely natural rubber latex, vinyl, nitrile and other materials (e.g., neoprene or polyisoprene). Since entering the market in the early 1990s, nitrile gloves have been the preferred glove type for use in the medical field. Compared to other common medical and surgical gloves (e.g., latex and vinyl), nitrile gloves cause fewer allergic reactions, are more tear-resistant, and are lower priced [3].

Even with the high demand for nitrile gloves, up to 15% of these products might still be rejected during quality control, due to the strict regulations for nitrile glove products. The largest defects come from latex dipping, which leaves craters, blisters, and pinholes. Air bubbles and dirt entrapped in the latex

compound and a greasy former are the main causes of these defects. Therefore, glove industries have a major disposal problem in dealing with rejected gloves. Nitrile gloves are similar to other rubber products in being non-degradable materials considered a potential feedstock for reclaiming rubber [4-5]. Scrap nitrile gloves are considered waste and are usually discarded. However, recycling is one of the best options to solve scrap disposal problems [6]. The utilisation of rubber waste has been adopted in several applications within the rubber and plastic industries, as well as in construction and building materials, and in-home decorations [7]. Converting nitrile gloves to a rubber matrix with potential for rubber products is crucial. This can be done by blending it with virgin rubber to gain synergistic properties [8]. Blending is also an easy and cost-effective method to produce new combinations of properties. Blends of natural rubber (NR)/recycled nitrile rubber (r-NBR) have been reported previously; however, those studies had a limited scope, focusing on the compounding and mechanical properties of the blends. However, this blend is incompatible and has poor interfacial adhesion between the phases [9]. Interfacial adhesion may be improved by replacing NR with a modified NR that either interacts chemically with both phases or has a specific interaction with one phase and a physical

interaction with the other. This phenomenon can be justified as an improvement in the compatibility of the blend. Commonly, compatibility can lead to a finer phase structure and enhanced interfacial adhesion, which improves the final characteristics of the blend.

To widen the use of this blend component, Epoxidized Natural Rubber, or ENR, has replaced NR. ENR is a chemically modified form of cis-1,4-polyisoprene rubber, whereby some of the unsaturation is converted into epoxide groups which are randomly distributed along the polymer chain [10]. ENR is known as a compatibiliser for incompatible blends and a processing aid. The incorporation of ENR-50 into rubber blends improves processability, stiffness, and resilience and also shows excellent oil resistance, reduced air permeability, good damping, and wet grip performance. This work assessed the effects of various blend ratios of NR/r-NBR and ENR/r-NBR on the thermal stability of the blends. The aim of this study was to gain better durability of the blends and to increase the life span of these rubber products.

EXPERIMENTAL

Materials

The main rubber matrices were NR and r-NBR. The SMR L Grade of NR was supplied by Mardec Berhad, Malaysia. ENR with 50% epoxidation (ENR50) was manufactured by Muang Mai Guthrie Public Company Limited, Phuket, Thailand. Juara One Resources Sdn. Bhd., Penang, Malaysia, supplied the r-NBR obtained from rejected nitrile gloves. Figure 1 summarizes the

steps involved in preparing the r-NBR for use. Pre-grinding of the r-NBR with a two-roll mill was followed by mechanical grinding using a Table Type Pulverizing Machine from Rong Tsong Precision Technology Co. Ltd. to obtain recycled rubber powder. The r-NBR powder was sieved using an Endecotts sieve. Then, the particle size of the recycled NBR was analysed using a SYMPATEC HELOS/BF Particle Size Analyzer. Figure 1 also shows the particle size analysis result for the recycled NBR sample. It shows that the distribution of particle sizes was between 125.74 μm and 558.03 μm . The d_{50} of the sample was 293.51 μm . Therefore, the mean particle size of r-NBR was 293.51 μm . The N330 grade carbon black used as a reinforcing filler was purchased from Malayan Carbon (M) Ltd. Other additives such as an activator (zinc oxide and stearic acid), an accelerator (*N*-cyclohexyl-2-benzothiazolesulphenamide, CBS), an antidegradant (*N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine, IPPD), and a curing agent (sulphur) were supplied by Bayer (M) Ltd, Petaling Jaya, Malaysia.

Preparation of the Blends

The aim of this study was to make a comparison between the use of NR and ENR as blending components for r-NBR. Various blending ratios for these two blends were prepared using a laboratory-sized two-roll mill (160 mm \times 320 mm), model XK-160, following ASTM method D3184. The blend formulations are given in Table 1. After compounding, the resultant compounds were compression moulded at 10 MPa each for their respective cure time (t_{90}) as determined with a rheometer.

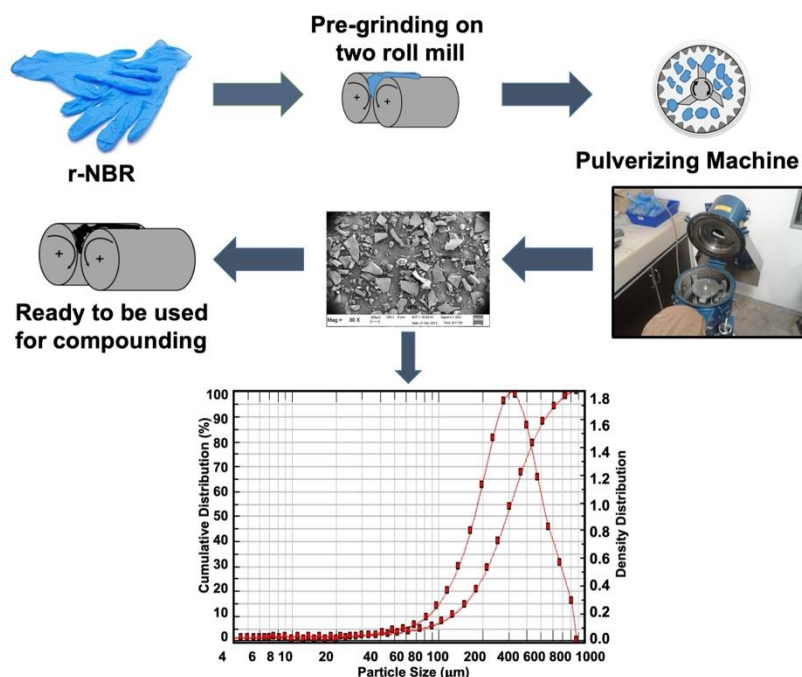


Figure 1. Schematic illustration of nitrile glove waste preparation and its corresponding characterization.

Table 1. The formulation of NR/r-NBR and ENR/r-NBR blends.

Ingredient	Amount (phr)	
NR/r-NBR	95/5, 90/10, 85/15, 75/25 & 65/35	-
ENR/r-NBR	-	95/5, 90/10, 85/15, 75/25 & 65/35
Zinc oxide	5	5
Stearic acid	2	2
CBS	1.5	1.5
IPPD	2	2
Sulphur	2	2
N330	30	30

Fourier Transform Infrared Spectroscopy (FTIR)

Changes in the chemical functionalities of the samples before and after natural weathering were determined by FTIR (Perkin Elmer 2000). All spectra were obtained using attenuated total reflectance (ATR) in transmittance mode from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} .

Measurement of Mechanical Properties

Dumbbell-shaped test samples were cut from the moulded sheets and prepared according to ASTM D3182. The tensile test was performed according to ASTM D412, at a crosshead speed of 500 mm/min using a universal tensile tester machine (Instron 3366).

Thermo-oxidative Ageing

The heat ageing of rubber blends was done according to ASTM D573. The dumbbell samples were placed in a circulating air oven (Thermolyne-oven series 9000) at 70 °C for 48 h and 168 h. The heat resistance of a rubber blend was evaluated based on the retention of its tensile properties, calculated as follows:

$$\text{Retention (\%)} = \frac{\text{Value after aging}}{\text{Value before aging}} \times 100 \quad (1)$$

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the NR/r-NBR and ENR/r-NBR blends was carried out with a Perkin-Elmer Pyris 6 TGA analyser. The samples were

scanned from 30 °C to 600 °C under a nitrogen flow of 30 ml/min, at a heating rate of 20 °C/min.

RESULTS AND DISCUSSION

Functionalities of the Blends

The chemical functionalities of raw NR, r-NBR, and ENR were characterized using FTIR as shown in Figure 2. The absorption peaks at 2920 to 2850 cm^{-1} were assigned to C-H stretching vibrations. The peaks at 1448 and 1375 cm^{-1} were attributed to $-\text{CH}_2$ and C-H deformations respectively. In r-NBR, a peak at 2230 cm^{-1} was assigned to CN and the connected bond of $\text{C}\equiv\text{N}$ -. On comparing NR and ENR, new peaks were observed at 873 and 1250 cm^{-1} , which were attributed to the stretching and deformation vibrations of the epoxy group on the NR molecular chain. The FTIR spectra of the NR/r-NBR and ENR/r-NBR blends are shown in Figure 3. Similar absorption peaks at 2913 and 2846 cm^{-1} were observed. The peaks at 3781 and 1536 cm^{-1} were assigned to the OH functional group and the $-\text{C}=\text{C}-$ chemical bond, respectively, in the structure of NBR rubber [11]. According to the rubber standards and the characterisation of acrylonitrile butadiene rubber, the peak at 1008 cm^{-1} was related to the $-\text{CH}=\text{CH}$ (trans) bond. The difference between ENR and NR as blending components was observed in the ENR peaks at 873 and 837 cm^{-1} [12]. Replacing NR with ENR showed that the mole percent absorbance of epoxide increased while the absorbance of the $=\text{C}-\text{H}$ deformation decreased.

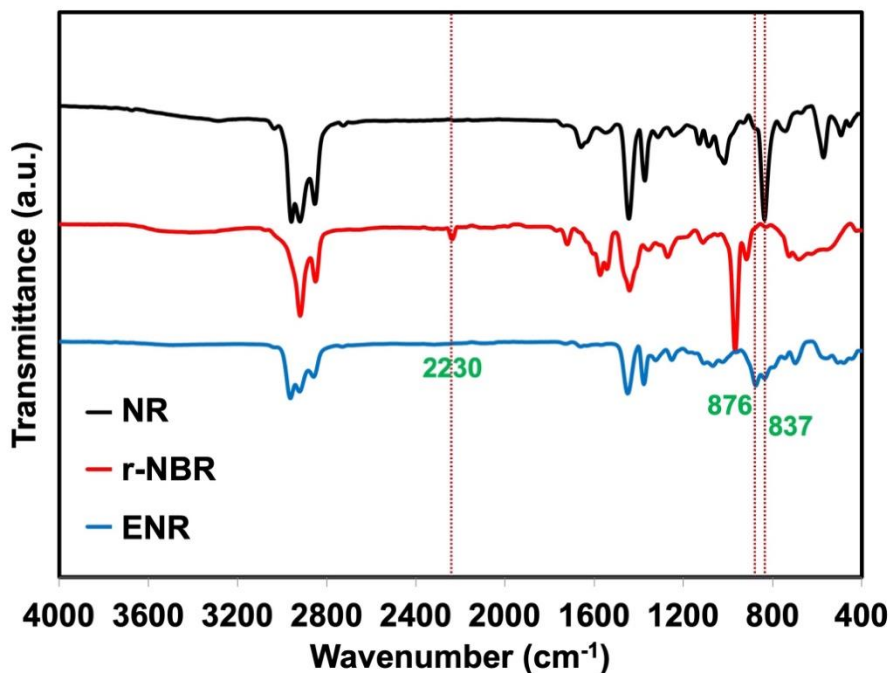


Figure 2. FTIR spectra of NR/r-NBR and ENR/r-NBR blends.

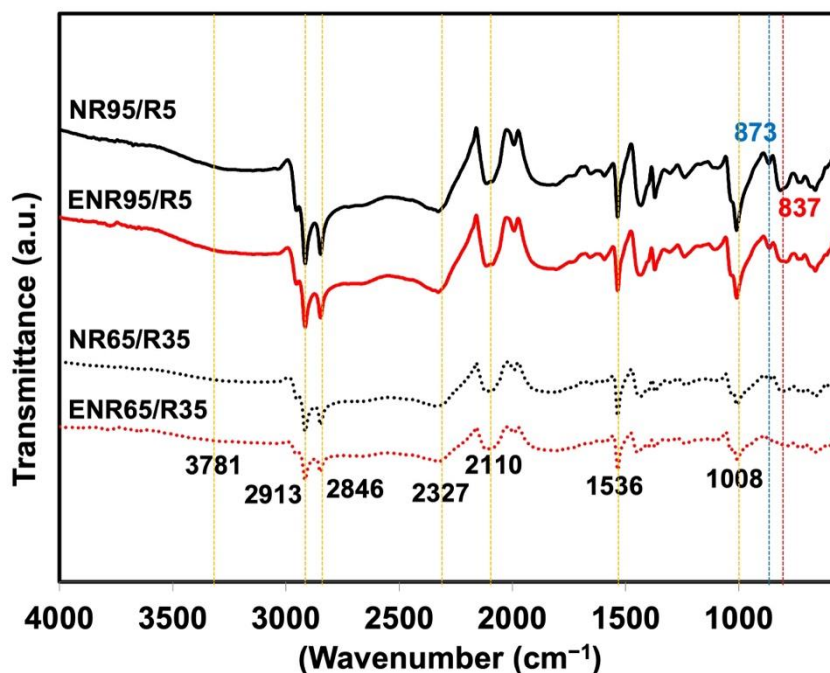


Figure 3. FTIR spectra of NR/r-NBR and ENR/r-NBR blends.

Thermo-oxidative Ageing

The effects of blend composition on the tensile strength of the NR/r-NBR and ENR/r-NBR blends are shown in Figure 4A. The tensile strength decreased with increasing r-NBR in both blends. The decrease in tensile strength was due to the incompatibility of the blends and poor dispersion of r-NBR in the NR and

ENR matrix because of the presence of a crosslink precursor in the rubber phase. When more r-NBR was added to the blends, compatibility was reduced. However, at the same blend ratio, the tensile strength of ENR/r-NBR blends was higher than that of the NR/r-NBR blends. This was due to the rubber blend becoming more rigid and stiff with increasing r-NBR content. ENR and r-NBR are polar rubbers, whereas

NR is a non-polar rubber. It has been generally observed that the mechanical response of a blend is closely related to its compatibility, and a synergistic effect is often obtained with miscible or partially compatible blends. The partial compatibility might be due to the hydrogen bonding interaction between r-NBR and the epoxy group of ENR-50. Figure 5A shows the decreasing trend of elongation at break for NR/r-NBR and ENR/r-NBR blends with increasing r-NBR content. This trend was due to the lower molecular weight and presence of a reinforcing filler in the r-NBR, which restricted the mobility of the rubber matrix and recycled rubber chains, causing the sample to fail at lower elongation. The decrease in elongation at break values was due to the decreasing effect of strain-induced crystallisation of NR and ENR as the recycled NBR content was increased. When the r-NBR loading was increased, weak interactions between the recycled NBR and the NR matrix were responsible for the deterioration of tensile strength and increase in the agglomeration of r-NBR, resulting in a decrease in elongation at break values. However, at the same blend ratio, the elongation at break values for the NR/r-NBR blends was higher compared to the ENR/r-NBR blends. This may be due to compatibility and better interaction between blends, which enable them to elongate at higher strain. Another reason

may be the lower flexibility of ENR as epoxidation increases the T_g and rigidity of ENR [13,14]. This has led to a higher modulus of the blends containing ENR. Noriman et al. [15] also found the same trend when they blended recycled NBR with styrene butadiene rubber, (SBR). From the morphology of the blends, recycled NBR exhibited a weak matrix interaction particularly when more than 15 phr of recycled NBR was used, thus decreasing the mechanical properties of the blends.

The tensile strength and elongation at break values for all aged samples decreased upon thermal ageing (see Figures 4B and 5B). At a fixed blend ratio, a reduction in tensile strength could be attributed to oxidation of the polymer, which results in chain scissions. Scission of larger molecular chains in a polymer increases the number of shorter chains which leads to fewer entanglements, thus decreasing its tensile strength as well as elongation at break values. The retained property percentage e.g., retained elongation, and retained tensile strength after thermal ageing was used to evaluate thermal stability. The retained tensile strength of both blends was lower for recycled NBR concentrations below 5 phr, but increased for blends with more than 30 phr of recycled NBR.

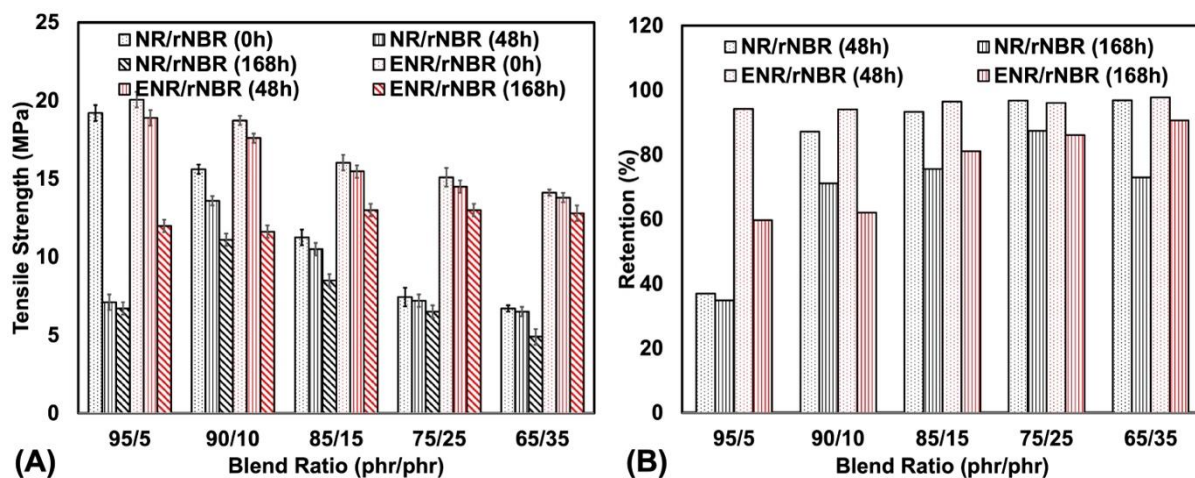


Figure 4. Tensile strength (A) and corresponding retention (B) as a function of blend ratios for NR/r-NBR and ENR/r-NBR blends.

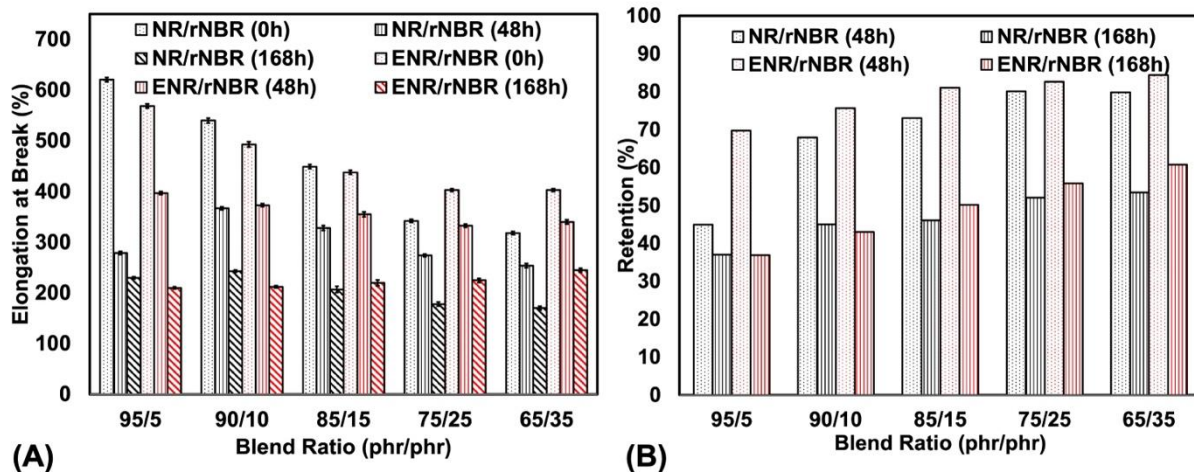


Figure 5. Elongation at break (A) and corresponding retention (B) as a function of blend ratios for NR/r-NBR and ENR/r-NBR blends.

Modulus is affected by several factors, such as surface reactivity which determines the polymer-filler interaction, aggregates, size and shape of particles, structure, and filler particle dispersion in rubber. Figure 6A shows the variation in modulus for M100 (at 100% elongation). The results indicate that M100 increased with recycled NBR content. This might be due to the increase in the crosslink density of both blends. As the content of r-NBR increases, the blends become stiffer, indicating an increase in modulus. At the same time, there is a decrease in elongation at break values. The incorporation of r-NBR into the rubber matrix increased the stiffness of the vulcanizates, as the tensile modulus represents material stiffness. However, at the same blend ratio,

ENR/r-NBR blends had a higher modulus than NR/r-NBR blends. This behaviour is attributed to the presence of ether crosslinks stemming from acid-catalysed ring-opening reactions in the ENR compound. The ability of mutual rubber reinforcement indicated by the rubber blend and better rubber-filler interactions determine the strength of the rubber blend. It was also found that the modulus of aged blends increased with increasing r-NBR content (see Figure 6B). This was probably due to the formation of additional crosslinks. The increase in crosslink density after thermal ageing of the blends was strongly related to the high rate of radical termination in the bulk of the polymer; hence, the material was more cross-linked [16].

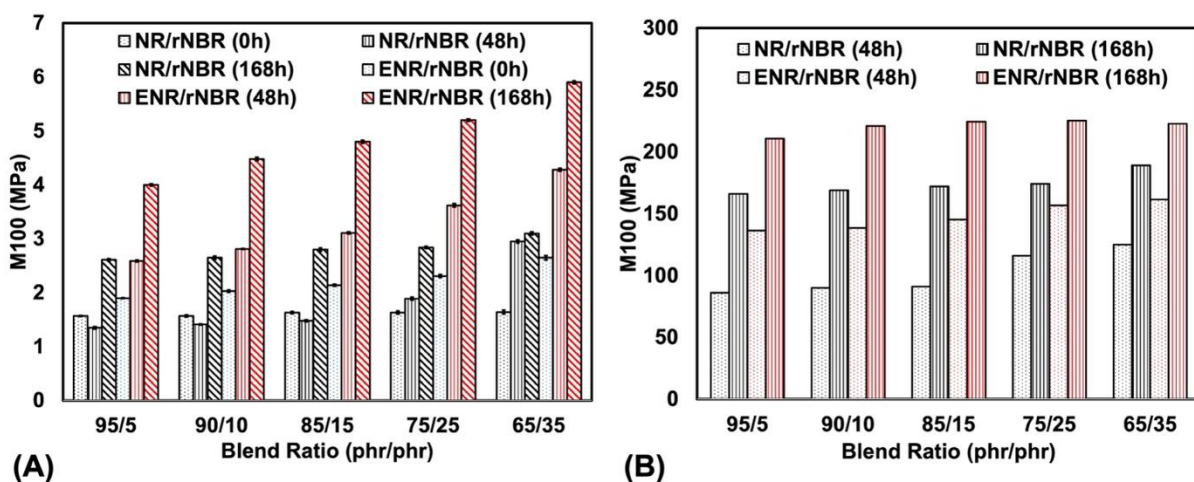


Figure 6. Stress at 100% strain (A) and corresponding retention (B) as a function of blend ratios of NR/r-NBR and ENR/r-NBR blends.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis measures mass change as a function of temperature in a controlled atmosphere. It is used primarily to determine the thermal and oxidative stabilities of materials and their compositional properties. The TG curves of raw NR, r-NBR and ENR are shown in Figure 7. The thermal stability of NR was the lowest, due to the unsaturation level of NR, making this rubber less thermally stable. Upon epoxidation (see ENR), the thermal stability became higher due to the replacement of the epoxy ring in the rubber molecule, which made ENR more resistant to heat. The r-NBR also showed slightly higher thermal stability than ENR, even though this rubber had been used prior to utilization. The thermal decomposition behaviour and derivative weight thermograms of the NR/r-NBR and ENR/r-NBR blends are shown in Figure 8. The decomposition temperature at different weight loss stages are summarised in Table 2. Two regions of degradation were evident for the blends. The initial minor weight loss at around 180–200 °C was due to the presence of

volatile matter such as stearic acid, and adsorbed water at around 300 °C [17]. The first step of degradation for both blends started at about 350 °C and was complete at around 480 °C. There were two regions of thermal degradation found in the DTG profiles of the NR/r-NBR blends (see Figure 8B). The blends containing low r-NBR content (NR95/R5) exhibited a small peak at the second stage, while a large peak was observed for blends containing a higher r-NBR content (NR65/R35). The first major degradation peak was due to the degradation of NR, while the second peak was due to the chain scission of r-NBR. The clearer peak corresponded well with a higher content of r-NBR. It is interesting to note that the ENR/r-NBR blends showed only one major DTG peak, unlike the NR/r-NBR blends. It was clear that the compatibility of the ENR/r-NBR blends was better than that of the NR/r-NBR blends. Better interfacial adhesion and compatibility of ENR and r-NBR created a homogenous mixture of the blend, which resulted in one major peak for thermal degradation [18]. These results also corresponded well with the thermal behaviour of raw rubbers, as shown in Figure 7.

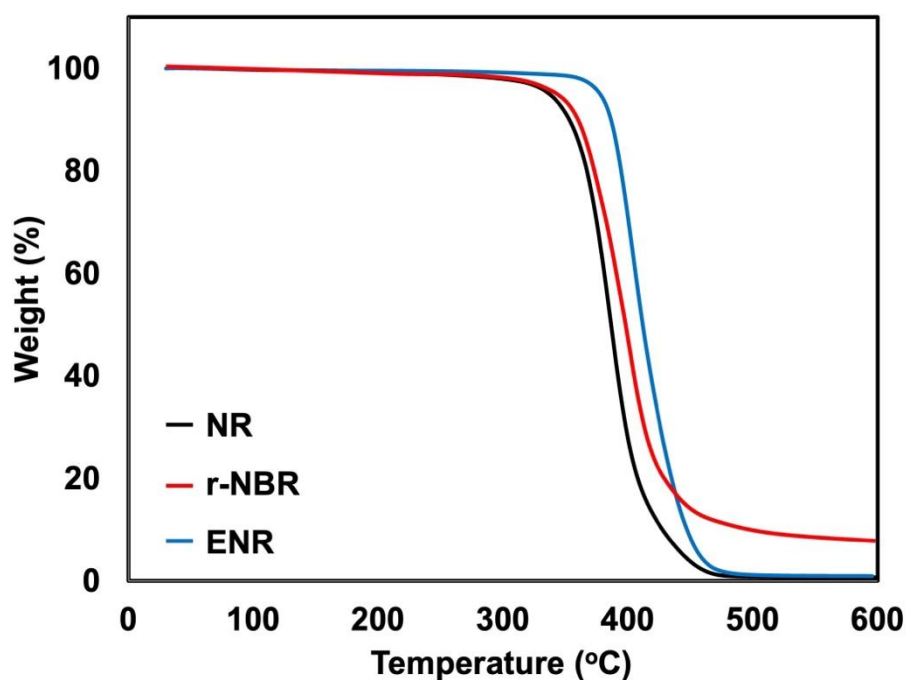


Figure 7. TG (A) and DTG (B) profiles of NR/r-NBR and ENR/r-NBR blends.

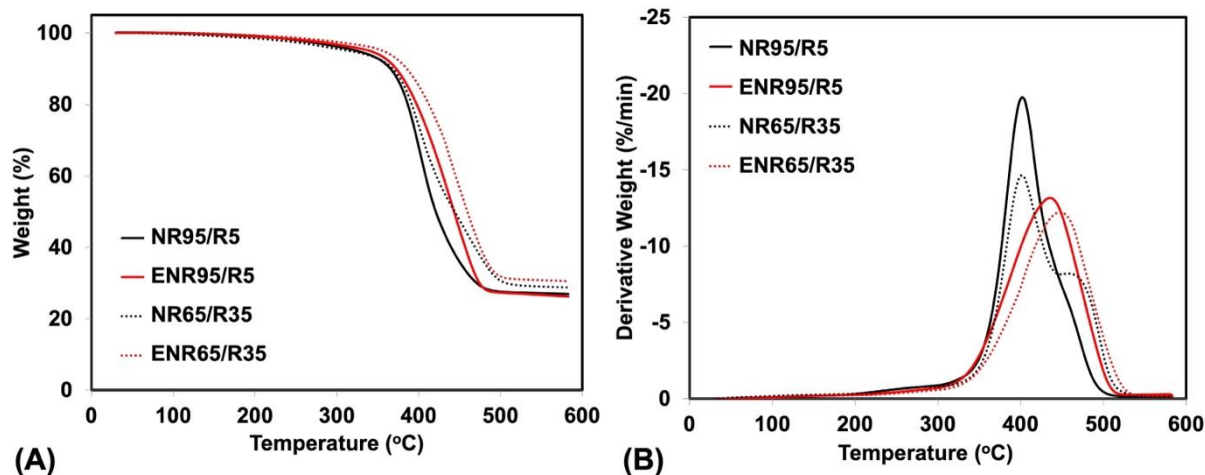


Figure 8. TG (A) and DTG (B) profiles of NR/r-NBR and ENR/r-NBR blends.

Table 2. Raw output from TG profiles of NR/r-NBR and ENR/r-NBR blends.

Blend (phr)	Maximum weight loss (%)	Temperature at 5% weight loss (°C)	Temperature at 50% weight loss (°C)	Temperature at maximum decomposition (°C)	Temperature at peak (°C)	Char residue (%)
NR95/R5	73.12	295	405	402	402	26.92
ENR95/R5	73.75	313	425	435	435	26.23
NR65/R35	71.32	296	414	401	401	28.69
ENR65/R35	69.46	330	438	447	447	30.55

Notably, the decomposition temperatures of the blends at 5 % and 50 % weight loss were found to be higher when the weight ratio of r-NBR increased. This was due to the higher thermal stability of r-NBR. The decomposition temperatures at various maximum peaks and the char residue of the blends are also presented in Table 2. The temperature at maximum weight loss for both blends increased with the increase in the weight ratio of r-NBR, suggesting that r-NBR was more thermally stable than NR or ENR. Better adhesion between ENR and r-NBR would contribute to a higher thermal stability by hindering the diffusion of volatile decomposition products [19, 20]. The char residue obtained for both blends at the final temperature increased as a function of the concentration of the r-NBR phase. As we have noted previously, nitrile glove waste may contain a small amount of filler. Thus, increasing the weight ratio of r-NBR led to a higher percentage of char residue.

CONCLUSION

The effect of blend ratios on the thermo-oxidative ageing and thermogravimetric analysis of NR/r-NBR blends was studied and compared with those of ENR/r-NBR blends. With a higher r-NBR weight ratio, the tensile strength and elongation at break

values decreased, whereas modulus values exhibited the opposite trend. r-NBR significantly improved the thermal stability of the blends by producing higher values for retention of tensile strength, elongation at break and initial decomposition temperature, as confirmed by the TGA results. This was because r-NBR consists of a crosslinked precursor and greater thermal resistance. At a similar blend ratio, ENR as a blending component was observed to have higher thermal stability than NR. This is because replacing epoxy rings on the rubber backbones gives ENR better resistance to heat ageing. In summary, ENR/r-NBR blends exhibited higher thermal stability than NR/r-NBR blends.

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