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Research Article

Influence of blend ratio on cure characteristics and tensile properties of nitrile butadiene rubber/devulcanized nitrile butadiene rubber glove (NBR/d-NBRg) blends

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Abstract
During the COVID-19 pandemic, Polish companies experienced an annual growth of about 6% in disposable protective gloves (DPG) production from 2014 to 2019. However, in March 2020, production surged by 30% compared to the same month in 2019. The increased demand for nitrile gloves raised environmental concerns due to the disposal of used gloves. A promising solution to this issue is the devulcanization of used nitrile rubber gloves (NBRg), which can be converted into useful materials. This study investigates the effects of blending devulcanized Nitrile Butadiene Rubber (d-NBRg) with NBR in different ratios on curing and mechanical properties. The rubber blends were prepared using a two-roll mill. Results showed that increasing d-NBRg content in the blends led to higher values of minimum torque (M_L), maximum torque (M_H), and delta torque (ΔM), indicating increased rigidity and stiffness due to a higher crosslink density. The vulcanization process was also accelerated with higher d-NBRg content, reducing scorch time (ts_2) and optimum cure time (t_{90}). Additionally, tensile strength improved significantly with increased d-NBRg content, attributed to the higher crosslink density, while elongation at break (EB)decreased due to reduced polymer chain mobility. Modulus at 100% elongation (M100), hardness, and density all increased as d-NBRg content increased.

Keywords: devulcanized nitrile butadiene rubber, nitrile butadiene rubber, curing, mechanical properties

Introduction

From 2014 to 2019, the production of disposable protective gloves (DPG) increased steadily each year by approximately 6% in Polish enterprises. However, in March 2020, compared to March 2019, there was a notable 30% increase in DPG production due to the pandemic [1]. Due to the increased need for personal protection equipment (PPE), this resulted in a noticeable increase in the manufacturing of rubber gloves, especially nitrile gloves. The pandemic's spike in the demand for rubber gloves, especially nitrile ones, also led to a rise in the quantity of rejected or discarded gloves, which created environmental problems and increased pollution and landfill trash. To mitigate these issues, the devulcanization process offers a sustainable solution by reversing the vulcanization of rubber, thereby enabling recycling and reusing of discarded gloves. Devulcanization is a process of breaking down crosslink network structures in the presence of devulcanizing agent [2], allowing worn rubber goods to be repurposed without losing their essential qualities, thus supporting environmental sustainability in rubber recycling efforts.

The blending of virgin rubber with devulcanized rubber represents an innovative approach in rubber technology, gaining the synergistic properties of blends with cost-effectiveness [3] and sustainability of recycled materials [4,5]. Blends of recycled nitrile rubber (d-NBRg) with virgin rubber such as natural rubber (NR) [6], NBR [7] as a rubber matrix were reported previously. However, there is a lack of previous studies on using d-NBRg in general rubber good products such as safety shoes and not much information on the performance and potential of d-NBRg from local industries in the rubber production. Many studies investigate the potential of d-NBRg as a filler in NR/SBR blends [8].

This study investigates the impact of devulcanized nitrile rubber glove (d-NBRg) on the properties of nitrile butadiene rubber (NBR) by incorporating varying amounts of d-NBRg, ranging from 30 phr to 70 phr, with 100 phr of NBR and d-NBRg serving as the control. The properties of the NBR/d-NBRg blends were evaluated via several tests, including cure characteristics, tensile, hardness, and density properties.

Materials and Methods

In this study, the primary rubbers used were devulcanized nitrile butadiene rubber gloves (d-NBRg) and nitrile butadiene rubber (NBR). The d-NBRg was supplied by Bridge Fields Resources Sdn Bhd, while Airelastic Industries Sdn Bhd provided carbon black N330 (CB), stearic acid (HST), and zinc oxide (ZnO). Mercaptobenzothiazole disulfide (MBTS) and tetramethylthiuram disulfide (TMTD) were used as accelerators for sulfur vulcanization, with sulfur serving as the vulcanizing agent and dioctyl terephthalate (DOTP) acting as a plasticizer.

Preparation of nitrile butadiene rubber/devulcanized nitrile butadiene rubber glove (NBR/d-NBRg) blends

NBR was mixed with d-NBRg in different ratios, as indicated in **Table 1**. A two-roll mill was used to mix all additives, and the mixing time was roughly ten minutes. Subsequently, the blends underwent compression at 150˚C and curing at a designated optimum cure time (t_{90}). In accordance with the testing, the blends were then cut into particular shapes.

Characterization

Cure characteristics measurement

The curing characteristics of the rubber blends were evaluated using Monsanto Moving Die Rheometer. Approximately 4 grams of sample from each formulation were analyzed at a temperature of 150 ± 2 °C and a pressure of 0.2 MPa. This testing was conducted according to the ASTM D5289 to obtain the minimum torque ($\mathrm{M_L}$), maximum torque ($\mathrm{M_H}$), scorch time ($\mathrm{t_{s2}}$), cure time ($\mathrm{t_{90}}$) and delta torque (ΔM).

Mechanical test

The results for tensile strength, elongation at break (EB), and modulus at 100 % elongation (M100) were obtained by conducting tensile test using Instron 5569 Series material testing machine at a crosshead speed of 500 mm/min according to ASTM D 412. The hardness was measured by using Wallace Tester Hardness (IRHD dead load) according to the ASTM D1415 and the unit was expressed in IRHD. The density test was conducted using Gravity Densimeter Electronic Density Tester, following the standards outlined in ASTM D792.

Table 1. Formulation of d-NBRg/NBR blends

Ingredients (phr)	Formulation (F)				
	F1	F2	F3	F4	F5
d-NBRg	0	30	50	70	100
NBR	100	70	50	30	0
CB	3	3	3	3	3
HST	3	3	3	3	3
MBTS	1	1	1	1	1
TMTD	0.3	0.3	0.3	0.3	0.3
Sulphur	2	2	2	2	2
ZnO	7	7	7	7	7
DOTP	3	3	3	3	3

phr: part per hundred

Results and Discussion

Cure characteristics

The cure characteristics of NBR/d-NBRg blends are summarized in **Table 2**. Unblended NBR (F1) and d-NBRg (F5) serve as controls for the blended NBR/d-NBRg samples, with F1 representing the lowest ML values and F5 representing the highest. A noticeable increase in values was observed with the introduction of d-NBRg into the NBR blends. This increase may be attributed to the higher viscosity of d-NBRg, which can lead to increased processability resistance [8]. The presence of curatives from the previous nitrile glove (NBRg) formulation contributes to this resistance, raising the viscosity of d-NBRg even after the devulcanization process. F1 exhibited the lowest MH and ΔM values, while F2 showed the highest. The incorporation of 30 phr of d-NBRg (F2) resulted in a significant increase of 106% in MH and 117% in ΔM compared to F1. Up to 30 phr of d-NBRg loading, the MH value decreased slightly by about 0.4% to 1.9% as compared to F2. However, the MH and ΔM values for the NBR/d-NBRg blends remained 102% and 12% higher, respectively, compared to both F1 and F5. The observed increase in ML and ΔM suggests an enhancement in rigidity, which can be attributed to a more compact network structure formed through crosslinking [9,10]. F1 exhibited the longest t_{s2}, whereas F5 showed the shortest. The increased number of free radicals in d-NBRg, along with formulation additives and amount of d-NBRg contents, likely contributed to the reduced t_{s2} of F5, thereby accelerating the vulcanization process. As the d-NBRg contents increased, t_{s2} decreased, which can be attributed to the faster crosslinking between the active free radicals in d-NBRg and the functional groups in NBR, leading to a reduction in both t_{s2} and t_{90} [8].

Mechanical properties

The tensile strength of d-NBRg/NBR blends is significantly influenced by the crosslink density and the presence of curatives. **Figure 1** illustrates the tensile strength of both unblended and blended d-NBRg/NBR. The lowest tensile strength is observed in F1, which is attributed to the low crosslink density of NBR and the minimal presence of curatives, compared to d-NBRg, which contains more curatives derived from the previous nitrile glove formulation and the additives in rubber formulation used in this project. This is further supported by the low values of ΔM. Additionally, the presence of active free radicals from short polymer chains, formed during the breakdown of the crosslink network in the devulcanization process of d-NBRg, contributes to an increase in crosslink formation in the vulcanized rubber, as seen in F2, F3, F4, and F5 [9].

Tensile strength increases with higher d-NBRg content in the NBR matrix. Specifically, incorporating 30, 50, and 70 phr d-NBRg into NBR results in a tensile strength increase of approximately 160%, 163%, and 243%, respectively, compared to F1. This improvement is due to the high crosslink density of d-NBRg, which is a result of the reaction between the functional groups of NBR and the free radicals of short polymer chains in d-NBRg. F5, consisting entirely of unblended d-NBRg, exhibits the highest tensile strength due to the extensive crosslink network formed between the free radicals of short polymer chains and the curing agent [10].

Table 2. Cure characteristics of NBR/d-NBR blends

	Formulation (F)				
Properties	**F1**	**F2**	**F3**	**F4**	**F5**
M_L (dN-m)	1.20	1.67	2.39	3.22	3.82
M_H (dN-m)	8.58	17.73	17.38	17.65	15.52
ΔM (dN-m)	7.38	16.05	15.00	14.43	11.69
t_{s2} (min)	5.49	4.11	3.24	2.59	2.07
t_{90} (min)	16.07	8.63	7.25	7.35	7.47

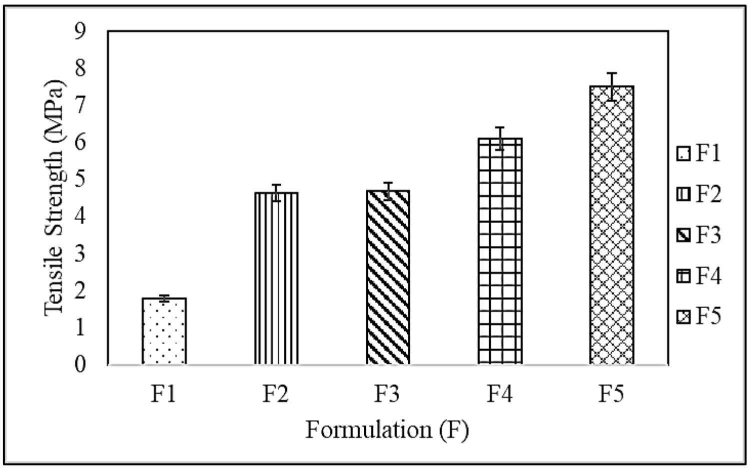

Figure 1. Tensile strength of NBR/d-NBRg blends

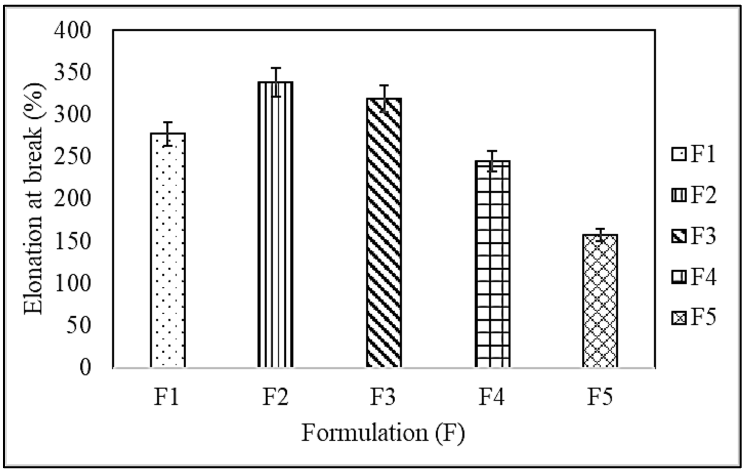

Figure 2. Elongation at break of d-NBRg/NBR blends

Figure 2 illustrates the effect of blending d-NBRg with NBR on elongation at break (EB), with F2 showing the highest EB and F5 the lowest. This trend demonstrates an inverse relationship between EB and tensile strength, of which higher crosslink density results in increased stiffness and reduced polymer chain mobility. The low EB in F5 indicates that its high crosslink density led to increased stiffness, limiting the flexibility of the rubber structure and reducing elongation at break. As the d-NBRg content increases from F2 to F4, EB decreases due to the rising crosslink density that restricts polymer chain mobility. In comparison, unblended NBR (F1) exhibits lower EB than the blended d-NBRg/NBR formulations (F2 and F3), which can be attributed to its lower crosslink density. Apart from that, the absence of curatives in unblended NBR impacts its resistance to elongation, reducing its flexibility. On the other hand, blending d-NBRg with NBR creates an uneven distribution of the crosslink network, further limiting flexibility. This pattern supports the general understanding that higher crosslink density in elastomer blends enhances stiffness but reduces flexibility, as demonstrated by the comparison between unblended NBR and the blended d-NBRg/NBR formulations.

The modulus at 100% elongation (M100), hardness, and density for d-NBRg, NBR, and their blends are shown in **Figures 3, 4, and 5**. These properties follow a similar trend, with values increasing as the proportion of d-NBRg in the blend rises. Specifically, the incorporation of d-NBRg into NBR resulted in increases in hardness, density, and M100 by approximately 1.7–10%, 37–43%, and 87–187%, respectively. This improvement in rigidity and stiffness is likely attributed to the presence of curatives and free radicals of short polymer chains in d-NBRg, which facilitate the formation of a more extensive crosslink network. As the content of d-NBRg increases in the NBR blend, the vulcanized structure becomes harder, leading to reduced chain mobility and enhanced overall rigidity [9].

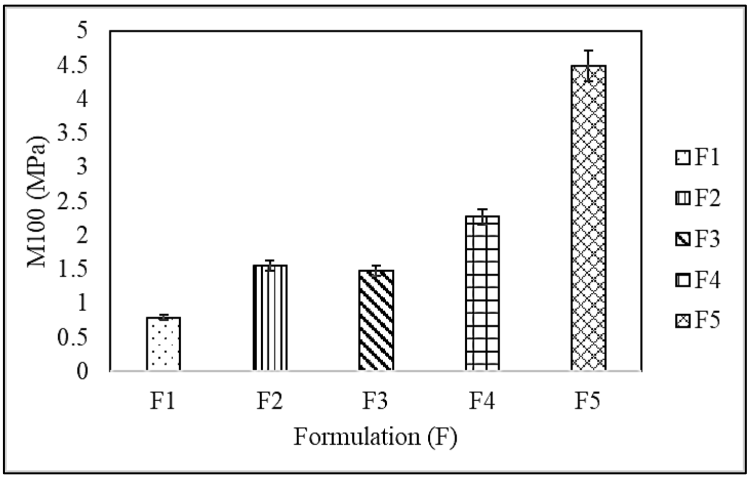

Figure 3. M100 0f d-NBR/NBR blends

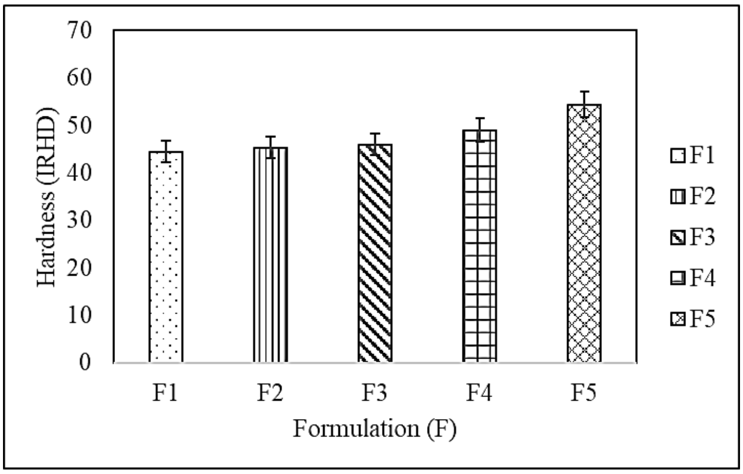

Figure 4. Hardness of d-NBRg/NBR blends

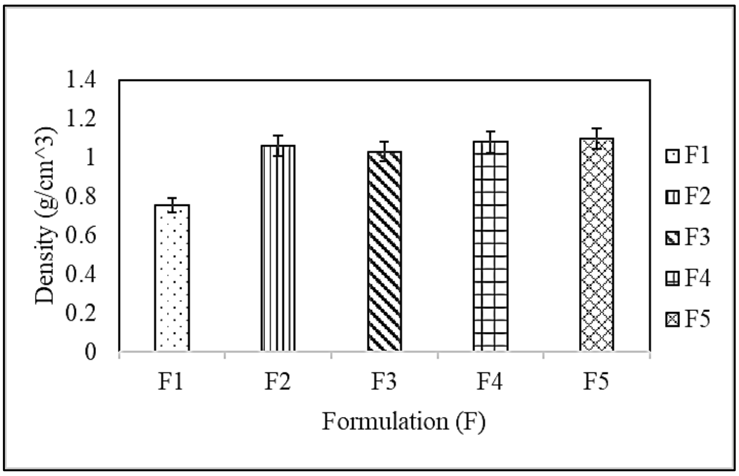

Figure 5. Density of d-NBRg/NBR blends

Conclusion

The incorporation of d-NBRg into NBR blends leads to significant improvements in mechanical properties. The study shows that increasing the d-NBRg content enhances curing characteristics, as evidenced by higher M_L and M_H values, alongside reduced ts_2 and t_{90}. Tensile strength shows a notable increase, with up to 243% enhancement compared to unblended NBR (F1), due to the formation of a denser crosslink network during curing. Concurrently, EB decreases, indicating higher stiffness and reduced flexibility as crosslink density increases. Furthermore, the M100, hardness, and density all increase with the d-NBRg content, showing a rise in rigidity and overall structural strength.

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