International Journal of Engineering & Technology, 7 (4.14) (2018) 322-325

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Effects of Epoxidised Natural Rubber on the Oil Resistance Property of NBR/ENR Blends used for Safety Footwear Application

H. Mohd Hanif, K.C. Yong*

Department of Engineering and Technology, Malaysian Rubber Board, Rubber Research Institute of Malaysia, 47000 Sungai Buloh, Selangor, Malaysia
**Corresponding author E-mail: kcyong@lgm.gov.my*

Abstract

Epoxidised natural rubber, ENR has emerged as a sustainable material for many applications due to its unique properties. This study sets out to investigate the effects of ENR on the oil resistance property of nitrile rubber, NBR composites used for safety footwear application. Blends of NBR/ENR i.e. 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 were prepared and tested for their oil resistance property and other physical properties such as hardness, tensile properties and abrasion loss. Results showed that varying the amount of ENR did not significantly affect the hardness and tensile properties of the composites. Nonetheless, it was found that ENR content highly influences the abrasion loss of the composites in which the abrasion resistance decreased with further addition of ENR contents. Despite the increase in oil swelling of the composites with increasing ENR content, the oil swelling values are considered low (< 5% volume change), indicating superior oil resistance property of the composites. These results confirm the possibility of ENR as a sustainable material for the production of eco-friendly composites with high oil resistance property for the footwear industry.

Keywords: *Epoxidised natural rubber; footwear; nitrile rubber; oil resistance; physical properties*.

1. Introduction

Safety footwear is a type of personal protective equipment (PPE) that is very important as it protects employees, usually those working in the heavy industry from impact, compression, dangerous chemicals, hot or slippery surfaces and other work-related hazards [1]. There are many types of safety footwear available in the market to cater to different types of occupational risks. Safety shoes are classified according to their features, which are labelled with relevant industrial symbols.

The sole of a safety shoe is usually made of synthetic polymers such as nitrile rubber (NBR), polyurethane (PU) and polyvinyl chloride (PVC). Besides of their good resistance to chemicals or oils and high storage longevity, synthetic polymers were also claimed to be light-weight and non-marking (non-streaking) on floors, compared to natural rubber (NR) based sole [2]. These properties make synthetic polymers desirable for shoe application. Nonetheless, there are some issues relating to these synthetic polymers. For instance, the use of PU as a base material for sole production may cause inhomogeneous filler distribution [2] which leads to poor physical properties. Polyester based PU has poor aging resistance due to hydrolysis which leads to embrittlement and cracking surfaces [3]. PVC and NBR have high hardness [2, 4] that may result in wearing discomfort and low slip resistance. In a survey, 35 % of the respondents rated their safety shoes as uncomfortable, which could result in injuries [5]. Other than that, the use of synthetic polymers such as PVC possesses dangers to the environment mainly attributed to the vinyl chloride monomer and the use of phthalates in the formulation [6]. Some European countries are even considering banning of PVC shoes as well as products containing phthalates to provide safer living environment [6].

Epoxidised natural rubber (ENR) is a modified form of cis-1,4-polyisoprene rubber in which epoxide groups are being introduced randomly to the unsaturated portion of the NR backbone. Two types of ENR that are commercially available are ENR 25 and ENR 50 which correspond to 25 % and 50 % epoxidation, respectively. The presence of epoxide groups enhances the properties of NR such as higher damping i.e. better wearing comfort, increase oil and oxidation resistance and higher abrasion resistance i.e. wearing resistance [2], [7]. These properties made ENR, an environmentally friendly and sustainable alternative to synthetic polymers that is suitable for sole production. Previously, ENR was used as a soling material to produce antistatic shoes and showed better properties in terms of conductivity, wearing comfort, and wearing resistance compared to conventional antistatic shoes [2].

In this study, the effects of ENR content on the properties of NBR based composites for safety footwear application were investigated. NBR is used as a soling material to produce soles that are oil resistant. The oil resistance property of nitrile rubber depends on its acrylonitrile content [8]. Blends of NR with NBR are commonly used to achieve a material that has high oil resistance while having good mechanical properties [9, 10]. However, the highly polar NBR may have poor compatibility with the non-polar NR due to their differences in polarity. Hence, the use of polar ENR instead of NR could improve the compatibility of the blends thus, enhancing their physical and chemical properties. The effects of ENR on NBR composites were studied on the oil resistance property and other important properties related to the soling material application such as tensile strength, hardness and abrasion. The findings of the study could suggest the potential use of ENR as an

Copyright © 2018 Authors. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

environmentally friendly and sustainable material for the production of composites with high oil resistance property for the safety footwear industry.

2. Experimental

2.1. Materials

Table 1: Formulation of NBR/ENR blends.

Ingredient (phr)/ Compound	1	2	3	4	5	6
NBR	100	90	80	70	60	50
ENR 50	0	10	20	30	40	50
Carbon black N330	20	20	20	20	20	20
Zinc oxide	5	5	5	5	5	5
Stearic acid	4	4	4	4	4	4
Antilux	1	1	1	1	1	1
Benzothiazole Disulfide (MBTS)	0.6	0.6	0.6	0.6	0.6	0.6
2-Mercaptobenzothiazole (MBT)	0.5	0.5	0.5	0.5	0.5	0.5
Tetramethylthiuram monosulfide (TMTM)	0.2	0.2	0.2	0.2	0.2	0.2
Sulfur	2	2	2	2	2	2

Epoxidised natural rubber, ENR of 50 % epoxidation level was obtained from Felda Rubber Industries Sdn Bhd. The nitrile rubber used was Nipol DN3350 produced by Zeon Chemicals. Carbon black of grade N330 was supplied by Cabot (M) Sdn. Bhd. Accelerators such as Benzothiazole Disulfide (MBTS), 2-Mercaptobenzothiazole (MBT), Tetramethylthiuram monosulfide (TMTM) were purchased from Galin Enterprise. Stearic acid and sulfur were obtained from Centre West Sdn. Bhd. whereas zinc oxide (transparent) was purchased from Bayer (M) Sdn. Bhd.

2.2. Sample preparation

Table 1 shows the formulation used in which the ENR content was varied from 0 to 50 phr. All compounding ingredients excluding the vulcanising agents were mixed in a Banbury 1600 internal mixer at a starting temperature of 70 ^{o}C with a rotor speed of 70 rpm. The resulting masterbatches were mixed with vulcanising agents with a two-roll mill at room temperature. Each compound was put under rheometer test to determine the curing time and later cured at 150 ^{o}C using a hot press.

2.3. Tensile test

Tensile test was carried out in accordance to ISO 37 method using an Instron universal testing machine. Results obtained include the tensile strength, tensile modulus and elongation at break of each composite.

2.4. Hardness test

The hardness of the composites was measured in triplicates by using a Shore A hardness durometer at room temperature.

2.5. DIN abrasion test

DIN abrasion test was conducted following the ISO 4649. The results obtained were expressed in the abrasion volume loss (mm^3).

2.6. Oil immersion test

The oil resistance of the composites were tested based on the ISO 1817 by immersing the composite in a fuel oil at room temperature for 22 hours. The percentage of volume changes of the composites after swelling in oil were recorded.

3. Results and discussion

3.1. Physical properties

The effects of ENR content on the tensile properties and hardness of NBR based composites are depicted in Table 2. Tensile properties signify the durability of a sole [11]. It was believed that materials with low tensile strength and elongation may crack or break due to flexing [3].

The tensile strength of pure NBR composite was 14 MPa. The tensile strength exhibited an increasing trend with further addition of ENR content. The maximum tensile strength recorded was 17 MPa at 30 -50 phr of ENR. A similar observation can be seen with the elongation at break in which the elongation at break was higher with composites containing ENR. The elongation at break of pure NBR composite (381 %) was increased up to 436 % with the addition of 50 phr ENR content. These results are in agreement with a previous study on ENR/NBR blends whereby blends with higher ENR content showed higher tensile strength and elongation at break [12]. One possible reason is due to the strain-induced crystallization effect of ENR [12]. Nonetheless, the changes in tensile strength and elongation at break were marginal and may not have practical significance. Tensile modulus at 100% elongation, M100 corresponds to the stiffness of the material. It can be seen that the tensile modulus of the composites were also not significantly different from each other.

Hardness measures the resistance to deformation produced by composite. It essentially indicates the impact absorption properties [13] hence, the wearing comfort [11] and the slip resistance of the shoes soles [14]. Sole with lower hardness has higher wearing comfort and higher slip resistance [14]. This is because softer soles have higher coefficient of friction that results in better grip or slip resistance [14]. As shown in Table 2, composite without ENR has the highest hardness (60 Shore A). Further addition of ENR resulted in a minimal but decreasing trend in the hardness of the composites. At the highest ENR content i.e. 50 phr, the hardness of the NBR/ENR blend was decreased to 57 Shore A. Other study had reported that further addition of ENR up to 60 phr caused a significant reduction in the hardness of PP/ENR blends [15]. The reduction in hardness could be attributed to the elastic property of ENR in the blend [15].

These findings suggest that varying the ENR content up to 50 phr has minimally improved the tensile properties and the hardness of the composites. Changing the concentration and the type of the reinforcing fillers such as the carbon black could result in a more prominent effect on these properties.

Table 2: Tensile properties and hardness of NBR/ENR blends.

Properties/ Compounds	NBR/ENR (100/0)	NBR/ENR (90/10)	NBR/ENR (80/20)	NBR/ENR (70/30)	NBR/ENR (60/40)	NBR/ENR (50/50)
Tensile strength (MPa)	14 ± 1	16 ± 1	15 ± 2	17 ± 4	17 ± 2	17 ± 3
Elongation at break (%)	381 ± 13	417 ± 42	407 ± 23	428 ± 55	384 ± 25	436 ± 34
Tensile modulus (MPa)	2.2 ± 0.1	2.2 ± 0.1	2.1 ± 0.1	2.1 ± 0.2	2.4 ± 0.3	2.0 ± 0.1
Hardness (Shore A)	60 ± 1	59 ± 1	58 ± 1	59 ± 1	58 ± 1	57 ± 1

3.2. Abrasion resistance

As footwear soles come in direct contact with the walking surface, some weight or volume of the material will be lost due to abrasion. This will affect the shape of the sole i.e. sole is worn out hence, making it uncomfortable for walking [3]. The DIN abrasion test was conducted to predict the wearing resistance of the composite which also corresponds to the life expectancy of the sole.

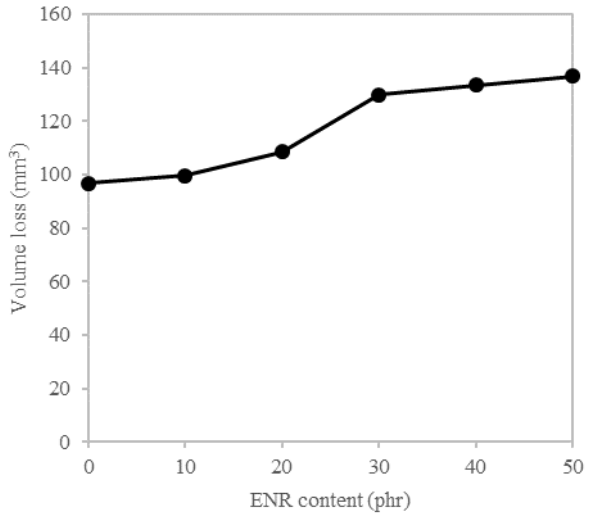

Fig. 1: Abrasion volume loss as a function of ENR content.

Results of the volume loss by abrasion are displayed in Figure 1. Pure NBR composite has a volume loss of 97 mm^3. The plot in Figure 1 shows that the volume loss was markedly increased from 97 mm^3 to 130 mm^3 with further addition of ENR content up to 30 phr. As the ENR composition increased beyond 30 phr, the volume loss was minimally increased, exhibiting an almost stagnant trend. The increase in abrasion loss with the addition of ENR suggests that the wearing resistance of the composites was decreased hence, shortened the life expectancy of the sole.

It was postulated that the abrasion loss in NR and styrene butadiene rubber (SBR) is mainly caused by mechanochemical attack rather than tearing failures due to the addition of carbon black which increases the strength and the stiffness of the polymers [16]. During abrasion, the main-chain rupture of NR and SBR produce radicals that react with oxygen causing the decomposition [16]. This could be the reason of the reduction in abrasion resistance of the NBR/ENR blends. However, different types of rubber such as the butadiene rubber (BR) shows better abrasion resistance because the radical forms due to the main-chain rupture reacts with the polymer itself. As a consequence, further crosslinking reaction happens rather than decomposition of the polymer [16]. This may be the reason of the incorporation of BR in some sole formulations, which is mainly to improve the abrasion loss [17] hence, the wearing resistance of the composite. Nonetheless, the addition of BR in shoe sole formulation is limited since it will significantly reduce the oil resistance property of the soling material due to the non-polar nature of the rubber.

Despite the increasing trend, at the highest ENR content of 50 phr, the volume loss of NBR/ENR composite was only 137 mm^3. This value is still within the acceptable range as required by the safety footwear industry in which the abrasion loss need to be less than 150 mm^3. Furthermore, according to a study, the abrasion resistance can also be improved by reducing the size of fillers from 1>µm to nm [18]. Therefore, the use of ENR up to 50 phr is suitable for the production of composites for safety shoe application.

3.3. Oil resistance property

NBR is chosen as a soling material for safety footwear production due to its superior oil resistance property. Resistance to oil is crucial as the physical properties of a swollen rubber are reduced by the presence of oil [19]. It was found that a 20 % change in volume due to oil swelling could cause up to 60 % reduction in properties such as hardness, stiffness and strength [20]. It was stated that the oil swelling values of ENR 50 fall between polychloroprene (CR) and a medium grade NBR, indicating good oil resistance property of ENR [7].

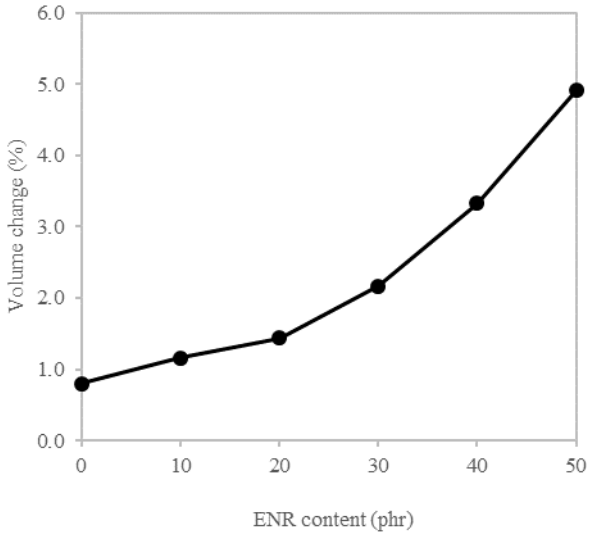

Fig. 2: Volume change of NBR/ENR composites after immersion in oil

Figure 2 displays the effect of ENR content on the oil resistance of the NBR/ENR blends. In this study, pure NBR composite has high oil resistance with less than 1% of volume change after being immersed in oil. It was reported that the increase in volume change of commercial NBR based soles after swelling in oil is range between 0.4 to 8.0 % [21]. As portrayed in Figure 2, the percentage of volume change increased with increasing composition of ENR which means that the oil resistance of the composites had decreased. This could be due to the introduction of the non-polar isoprene groups of ENR to the highly polar NBR which increase the compatibility of hydrocarbons with the blend hence, exacerbate its resistance to oil.

Nonetheless, the deterioration of oil resistance property by ENR is not severe since the difference in volume change between the NBR/ENR blend of 50:50 ratio with pure NBR composite was only 4%. The maximum percentage of increase in volume of the NBR/ENR blend by oil was only 4.9 %, which shows better oil resistance property compared to some commercial NBR based soles as reported by a previous study [21].

The results of the volume change also proved that the use of ENR significantly improve the oil resistance property of NR. NR is a non-oil resistant material. NR based soles recorded 60 – 87 % increase in volume change after being immersed in oil [21]. Previously, a research has shown that the NR/NBR blend (50:50) had a swelling percentage of 22.6% [22] which is almost five times higher than the one reported in this study. In other study, blends of ENR with recycled NBR (NBRr) also showed better oil resistance compared to NR/NBRr blends [23]. This is attributed to the presence of oxirane group which increases the polarity of ENR thus, its oil resistance property [23]. Another possible reason is due to the increase in solubility parameter of ENR as the level of epoxidation increases [24]. The smaller the difference in the solubility parameters between oils and rubbers, the better the solubility of the oil in the rubber i.e. higher oil uptake or swelling by rubber [25]. It was found that ENR 50 has the lowest swelling compared to ENR 10 -40 after being immersed in *n*-pentane which could be due to its higher solubility parameter [24]. According to Gelling *et al*. [26], the NR, ENR 26 and ENR 48 have a solubility parameter of 16.9, 17.4 and 18.2 $MPa^{1/2}$, respectively. Therefore, ENR 48 has higher difference in solubility with *n*-pentane (14.4 $MPa^{1/2}$) [26] compared to NR, which leads to lower *n*-pentane uptake [24]. As per the ISO 20345 standard, the change in volume swell by oil should not exceed the 12 % limit for safety footwear application. Since the maximum increase in volume by oil is less than 5%, it is evident that the NBR/ENR blends (up to 50 phr ENR) are ideal for the manufacturing of safety footwear that is highly oil-resistant and has better oil resistance property compared to some commercial NBR soles [21] and other NR/NBR blends [22].

4. Conclusion

The tensile properties, hardness, abrasion loss and most importantly, the oil resistance of NBR/ENR blends as a function of ENR content for safety footwear application have been established. Composites with ENR showed minimal but, improved tensile properties and softness. On the other hand, the abrasion loss exhibits an increasing trend with the increasing composition of ENR, suggesting the adverse effect of ENR on the wearing resistance of the composites. However, at the highest concentration of ENR (50 phr), the value of abrasion loss (137 mm^3) was still within the acceptable range for safety footwear application. The percentage of volume change by oil was found to be directly proportional to the concentration of ENR, implying a decrease in oil resistance of the composites. Nonetheless, the NBR/ENR blends (up to 50 phr ENR) are still considered highly oil-resistant as the maximum percentage of volume change by oil was only 5%, which is much lower than the 12 % limit as per the ISO 20345 standard. The findings of this study successfully confirm the potential of ENR as an environmentally friendly and sustainable material for the production of composites with high oil resistance property for safety footwear application.

Acknowledgement

The authors would like to thank the Malaysian Rubber Board for the financial support for this project. Assistance provided by Hassanal Baharom and Meor Syuhaidy is also highly appreciated.

References

[1] Moran MM, *Construction safety handbook*, ABS Consulting, (2003).
[2] Yong KC & Mohamad AA, Epoxidised natural rubber based blend for antistatic footwear application, US 2014/0194553 A1, (2014).
[3] Gnanasundaram S, Kannan S, Ranganathan M, Das BN & Mandal A B, Characterization of footwear soling materials based on biodegradable polyurethane, *Polymer – Plastics Techno. Eng*., 54, 15, (2015), 1585- 1595.
[4] Rapo-Brunet S, Shoe sole comprising a rubber composition based on nitrile-butadiene rubber, an oil and a resin, US 2014/0336311 A1, (2014).
[5] Akhbar-Khanzadeh F, Bisesi M S & Rivas R D, Comfort of personal protective equipment, *Appl. Ergonomics*, 26, 3, (1995), 195-198.
[6] Ames KA, Elastomers for shoe applications, *Rubber Chem. Technol*. 77, 3, (2004), 413–475.
[7] Gelling IR, Epoxidised natural rubber, *J. Nat. Rubber Res*., 271–295 (1991).
[8] Patil A O & Coolbaugh, T S, Elastomer: A literature review with emphasis on oil resistance, *Rubber chem. tech*., 78, 516-535.
[9] Sirisinha C, Baulek-Limcharoen S & Thunyarittikorn J, Relationships among blending conditions, size of dispersed phase, and oil resistance in natural rubber and nitrile rubber blends, *J. Appl. Polym. Sci*., 82, 5, (2001), 1232–1237.
[10] Clarke J, Clarke B, Freakley P K & Sutherland I, Compatibilising effect of carbon black on morphology of NR – NBR blends, 30, 1, (2001), 39–44.
[11] Mohan R, Raja S, Saraswathy G & Das B N, Surface modification of TPR sole : An approach in improve slip resistance on quarry and ceramic tiles, *Rubber Chem. Technol*., 88, 1, (2015), 163–175.
[12] Ismail H, Tan S & Poh B, Curing and mechanical properties of nitrile and natural rubber blends, *J. Elastomer and Plastics*, 33, 4, (2001), 251-262.
[13] Silva R M, Rodrigues J L, Pinto V V, Ferreira M J, Russo R & Pereira C M, Evaluation of shock absorption properties of rubber materials regarding footwear applications, *Polym. Test*., 28, 6, (2009), 642–647.
[14] Mohan R, Das B N & Sundaresan R, Effect of hardness and surface roughness on slip resistance of footwear rubber sole, *J. Test. Eval.*, 43, 6, (2015), 1574-1586.
[15] Mohamad N, Zainol N S, Rahim F F, Maulod H E A, Rahim T A, Shamsuri S R, Azam M A, Yaakub M Y, Abdollah M F & Manaf M E A, Mechanical and morphological properties of polypropylene/epoxidized natural rubber blends at various mixing ratio, *Procedia Eng*., 68, (2013), 439–445.
[16] Hong C K, Kim H, Ryu C, Nah C, Il Huh Y & Kaang S, Effects of particle size and structure of carbon blacks on the abrasion of filled elastomer compounds, *J. Mater. Sci.*, 42, 20, (2007), 8391–8399.
[17] Pyo K, Choi J, Lee C, Park C, Improvement of frictional property of BR/CIIR composite rubber for shoes outsoles, *Polym. Korea*, 37, 3, (2013), 255-261.
[18] Yuvaraj P, Rao J R, Fathima N N, Natchimuthu , Mohan R, Complete replacement of carbon black filler in rubber soles with CaO embedded activated carbon derived from tannery solid waste, *J. Cleaner Prod*., 170, (2018), 446-450.
[19] Southern E, Development in rubber technology- 1: Principles of product design, *Applied science publisher*, Essex, England, (1979), 249-278.
[20] Lachat V, Understanding oil resistance of nitrile rubber CN group interactions at interfaces, PhD Diss., University of Akron, (2011).
[21] Aschan C, Hirvonen M, Rajamaki E, Mannelin T, Slip resistance of oil resistant and non-oil resistant footwear outsoles in winter conditions, *Safety Science*, 45, (2005), 373-389.
[22] Yuniari A, Mayasari HE & Setyorini, I, Curing characteristics, swelling and mechanical properties of natural rubber/nitrile butadiene rubber blends with and without compatibilizer, *Journal of Leather, Rubber, and Plastics*, 33, 2, (2017), 65-72.
[23] Ahmad H S, Ismail H & Rashid A A, Hardness and swelling behaviour of epoxidized natural rubber/recycled acrylonitrile-butadiene rubber (ENR 50/NBRr) blends, *AIP Conf. Proc*., 1865, (2017), 040002.
[24] Kinasih N A, Fathurrohman M I & Winarto D A, Sweliing behaviour in n-pentane and mechanical properties of epoxidized natural rubber with different epoxide content, *IOP Conf. Ser.: Mater. Sci. Eng*., 223, (2017), 012002.
[25] Petchkaew A, Implications of non-carcinogenic pah-free extender oils in natural rubber based tire compounds, PhD Diss., University of Twente, (2015).
[26] Gelling I R, Tinker, A J & Abdul Rahman H, Solubility parameters of epoxidised natural rubber, *J. Nat. Rub. Res*, 6, 1, (1991), 184-205.