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ASSESSMENT OF THE BONDING PROPERTIES OF EPOXIDIZED NATURAL RUBBER (ENR-25) BASED ADHESIVES FILLED WITH CALCIUM CARBONATE FOR LEATHER AND FOOTWEAR APPLICATIONS

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ABSTRACT

The adhesion properties of epoxidized natural rubber (ENR 25 grade)-based adhesive was studied in the presence of calcium carbonate. The range of calcium carbonate loading was from 10 to 40 parts per hundred parts of rubber (phr). The footwear substrates: Microcellular (MC) Resin rubber (RR) and leather (LT) outsoles were used. The lap shear and peel strength were determined by a Llyod Adhesion Tester operating at 8cm/min. The assessment of the bonding strength, such as viscosity, peel strength, lap shear test, and as well as the effect of temperature and chemicals on the adhesive bonds were carried out on the outsoles using standard methods. FTIR result of the ENR compounds showed important characteristics peak confirming the presence of Epoxide group and $CaCO_3$. Results obtained shows that viscosity of ENR-based adhesives increases gradually with increase in calcium carbonate loading from 10-40phr due to the concentration effect of the filler. However, for lap shear and peel strength, it passes through a maximum at 30 phr loading of calcium carbonate, an observation which is attributed to the optimum wettability of adhesives on the substrate. Temperature had a slight effect on the peel and lap shear test. The adhesive showed good resistance to cold and hot water as the filler loading increases from10-40phr filler loading. The microcellular out- soles showed the best adhesion properties in terms of lap shear test and peel strength of the adhesive bonds. This is confirmed from the maximum results of 83.3N/m^2 and 458.3N/m^2 corresponding to peel and lap shear of the adhesive bonds respectively. The produced adhesive showed an expedient adhesion property which can be applied in footwear production.

KEYWORDS
Epoxidized natural rubber, calcium carbonate, adhesion, adhesives, microcellular, leather, outsoles, footwear

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INTRODUCTION

The adhesive has come a long way from a humble beginning. Glue in various forms has been used for over thousands of years to bond objects together. From tree beeswax are archeologist have discovered all different kinds of materials, that has been used as adhesive. Even with their primitive beginning. Adhesive have evolved and have grown into a multi-billion-dollar industry. Adhesive have become an integral part of our say today live there are various types of adhesive available derived from both natural and synthetics sources (Ebnesajjad, 2011). Adhesive is any substance that can hold materials together in functional manner by surface attachment that resists separation. Adhesive as a general term includes cement mucilage glue and paste terms that are often use interchangeably for any organic material that joins adhesive bond (Shrikant, 2018).

Epoxidized natural rubber (sometimes called Epoxyprene and abbreviated to ENR) has much improved heat and chemical resistance because the oxirane ring increases the hydrophilicity and reduces the number of double bonds in the backbone. Epoxidation also improves the miscibility with polar polymers. The three common levels of epoxidation are 50, 25 and 10 mole percent, referred to ENR-50, ENR-25 and ENR-10 respectively. ENR-50 undergoes strain crystallization like NR, but with oil resistance comparable to a medium acrylonitrile NBR and gas permeability similar to butyl rubbers. Silica reinforced ENR rubbers or blends with natural rubber have lower rolling resistance than NR and better wet traction than oil-extended styrene-butadiene rubber (OESBR) and have been considered.ENR-25 can be used in many applications where natural rubber is used but where improved Heat and oil resistance and/or lower gas permeability is required. Applications include anti vibration mounts, footwear components, tires, bearings, and adhesives (Poh, 2007).

Fillers are often used in adhesives in order to improve their properties, such as increasing hardness and to have reinforcing properties. Hence, the choice of the filler and its concentration are often critical. In addition, adhesion may also be affected by the filler's presence either due to absorption of coupling agents, change in rheological properties (reducing mechanical adhesion) or changing moisture permeability which affects hydrolytic changes at the interphase. It has been shown that in pressure sensitive adhesives, fillers may affect properties such as cohesion, cold flow and peel adhesion. Most fillers increase cohesion and reduce cold flow, fillers are usually used in epoxy adhesives for many different purposes. They can be used to increase thermal conductivity, improve corrosion resistance, reduce shrinkage during cure, and sometimes to reduce cost. Some examples of fillers in epoxy adhesives are the ones used to increase wear resistance in thin layer coatings (Hashim & Ong, 2014)

Poh *et al*. (2008) studied on the adhesion property of epoxidized natural rubber (ENR)based adhesives containing calcium carbonate. The result shows the viscosity is the dependent of adhesive and calcium carbonate concentration. For both adhesives, viscosity increase gradually with increase in calcium carbonate loading. For all the loadings of the filler ENR 25 consistently indicated higher viscosity compared to that of ENR 50. The phenomena may be explained by the stronger interaction (i.e. H-bonding) between ENR 25 and calcium carbonate filler. ENR 25 which has a lower Tg (i.e -45^{0}C) interact better with the filler due to its greater flexibility compared to ENR 50 (Tg=-20ºC), therefore, based on this report, this research adopted the use of only ENR-25 as the based material to produce the adhesive.

In another study, Poh and Saari (2011) also reported on the adhesion properties of epoxidized natural (ENR-50)-based adhesives in the presence of Magnesium Oxides, using PET as the substrate. The calcium carbonate is therefore a chemical compound with the formula $CaCO_3$ is common substance found in rocks as the minerals calcite and aragonite most notable as limestone which is type of sedimentary rock consisting mainly of calcite and is the main component of egg shell, snail shell, sea shell, and pearls. Calcium carbonate is achieved ingredient in agricultural line and is create when calcium irons is in hard water react with carbonate ion to create lime scale. It has medical use as a calcium supplement or as anti-acid. But excessive consumption can hazardous and course poor digestion (Poh *et al*., 2008). This research further investigates the adhesion/bonding properties of ENR-25 based adhesives filled calcium carbonate for footwear applications using different outsoles as substrates.

MATERIALS AND METHODS

The epoxidized natural (ENR-25) having 25mole% of epoxidation, used as the elastomer, was ordered from Zayo Sigma chemicals Abuja, Nigeria source Epoxyperene-25 (Standard Malaysian rubber). Other chemicals/regent grades were obtained from chemical stores in Zaria. The footwear out-soles; Microcellular (MC), Resin Rubber (RR) and leather (LT) were obtained from the

Department of Footwear Technology, Nigerian Institute of Leather and Science Technology (NILEST) Zaria, Nigeria. The tackifier used was Arabic gum, toluene was used as the solvent throughout the study, and precipitated calcium carbonate with mean particle size of 10um was used as a filler. All these were commercial grade materials and they were used as supplied.

Compounding of the ENR-$CaCO_3$

The ENR-25 was compounded using a two-roll mill at a temperature of 50ºC. The calcium carbonate (Filler) was added at various filler loading of 5g, 10g, 15g, 20g; equivalent to 10, 20, 30 and 40, phr of ENR-25. The compounded sample after mastication were collected and characterized.

Preparation of ENR-25 $CaCO_3$ adhesives

30g each of the masticated ENR-25 was dissolved in 120 ml of toluene, the rubber solution wLLas then left overnight to ensure complete dissolution. Other additives such as sodium oleate and diphenyl amine were added with constant steering. 4g of tackifer (Arabic Gum) corresponding to 80phr of resin was added to the rubber solution. For comparison purpose, one control sample was also prepared without calcium carbonate, using the same formulation. (Poh *et al*, 2008) **Table 1:** Formulation table for the preparation of ENR-$CaCO_3$ adhesive

		Formulation(phr)				
S/N	Ingredient	A	B	C	D	E
1	ENR	100	100	100	100	100
2	Toluene	120	120	120	120	120
3	$CaCo_3$	0	10	20	30	40
4	Sodium oleate	10	10	10	10	10
5	Diphenylamine	1	1	1	1	1
6	Arabic gum	80	80	80	80	80

Application of ENR-$CaCO_3$ adhesives on footwear outsoles

The ENR adhesive was applied on both surfaces of the outsoles (microcellular, Resin rubber and leather), for several minutes using a hand brush at coating area of 8cm x 3cm. The samples were then air dried at 30°C for 24hours to eliminate the toluene after which they were stuck together using a manual pressure machine until they have a strong bond almost immediately.

Testing/characterization

FITR analysis of ENR compounds

The FTIR Spectra of the ENR and ENR filled CaCO3 adhesives were obtained using FTIR spectrophotometer at a wavelength of 600-4000cm^{-1}.

Adhesion properties

T- Peel Test ASTM D-903 of the ENR-$CaCO_3$ adhesive

T- Peel test is commonly used to measure the adhesive strength between the bonded surface of two flexible substrate or a flexible and rigid substrate by a means of a T-type specimen. The flexible substrate often consists of tape film thin plastic material, rubber, or other polymers whereas the rigid substrate is commonly but not limited to a type of metal, rigid plastic or composite. The T-peel test (ASTM D-903) was carried out using a Lloyd adhesion tester on the Microcellular (MC), Resin rubber (RR) and Leather outsoles (LT) outsoles.

Lap Shear Strength ASTM D-10021 of ENR-$CaCO_3$ adhesives

Lap shear strength testing measure the ability of a material to withstand stresses set in a plane, or wood, where the exerted shear force is moving the two substrates in opposite's direction. It is one of the most common stresses that a bonded joint can face during services, especially in structural bonding applications. The lap shear test (ASTM D10021), was performed on the Microcellular, (MC), Resin rubber (RR), and Leather (LT), outsoles.

Viscosity test

The viscosity of the adhesive sample was measured using a Mooney Viscometer according to the procedure described in ASTM D-907. The viscosity of adhesives the sample was determined at temperatures of 40 and 100°C, in the following ways; first, spindle 3 was selected, the sample was then transferred to a 120ml beaker. The spindle was attached to the upper coupling by holding the coupling between the thumb and forefinger while cautiously rotating the spindle counterclockwise. The spindle was immersed into the sample up to the middle of the indentation in the shaft. The viscometer was then turned on and allowed to run until a constant reading was obtained. This reading was taken as the viscosity of the sample adhesive in Cp.

Effect of Temperature on Peel test and Lap Shear Test

Using the same ASTM standards, the effect of temperature on the peel and lap shear test of the ENR-$CaCO_3$ adhesives were determined using Lloyd adhesion tester by varying temperature range of the machine from 30ºC, 35ºC to 40ºC respectively.

Chemical Resistance

The chemical resistance test for the microcellular (MC) outsoles were conducted according to the procedure described by Sandip *et al*. (2003). The outsoles bonded with the ENR- adhesives were immersed in cold water (30ºC) for 1 day after which they were taken out, dried at temperature (30ºC and 50% + 5% RH), for 1 day and subjected to lap shear and peel tests. A separate group of bonded shoe soles (MC) pieces were immersed in hot water at 100ºC for 1hr, another group in water at pH2 (acids) and another group of pH10 (alkali) at 80ºC for 1hr, after which the lap shear strength and peel strength were determined.

RESULTS AND DISCUSSION

FTIR

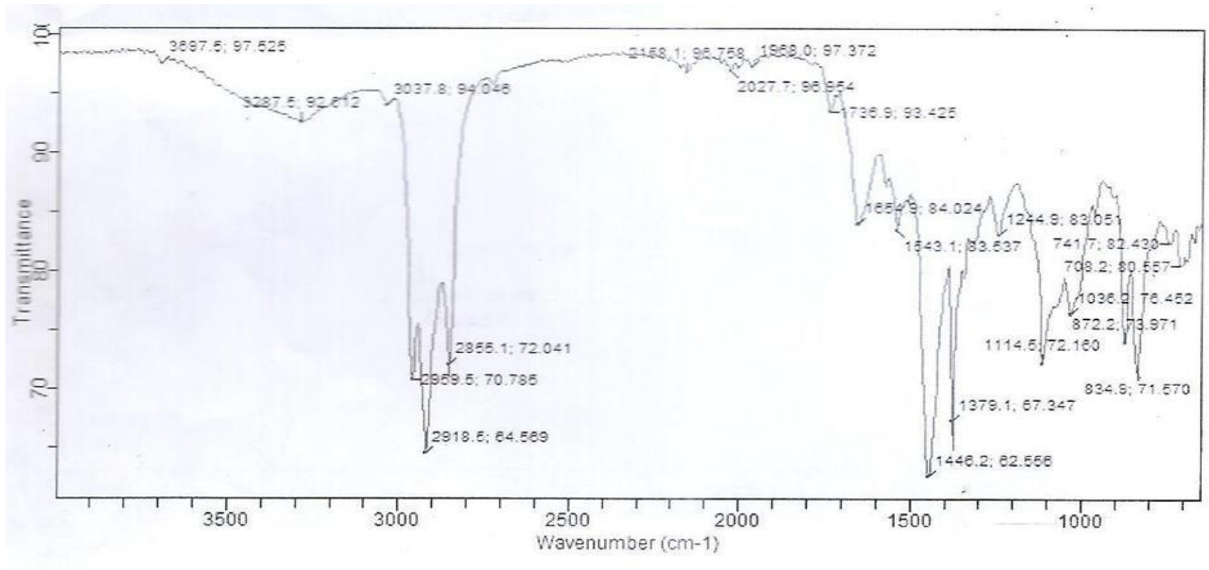

Figure 1: FTIR spectra of epoxidized natural rubber (ENR-25) without $CaCO_3$ filler

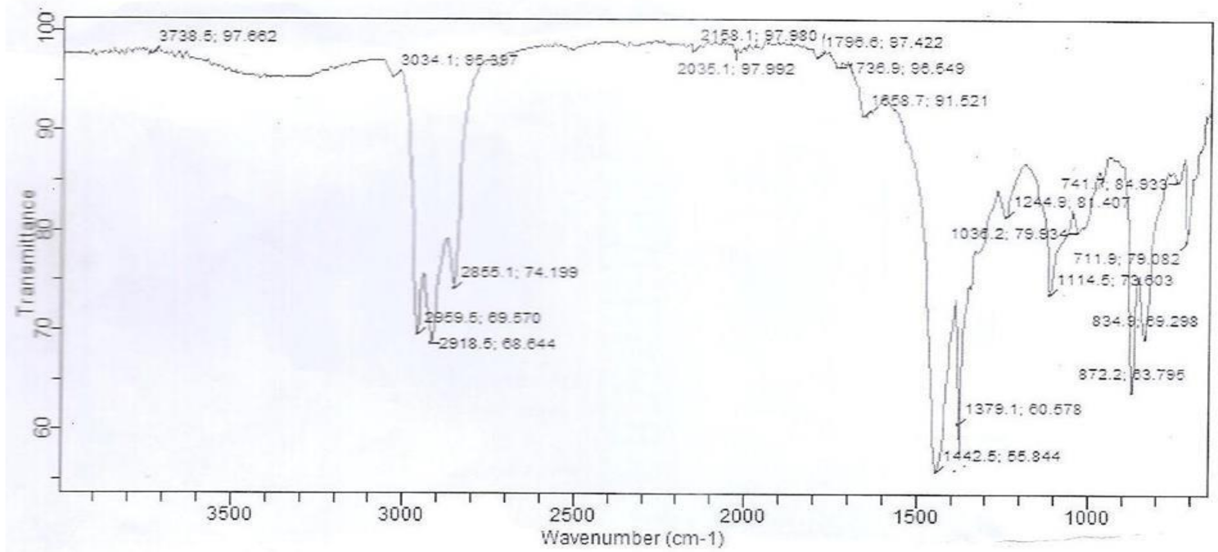

Figure 2: FTIR result of ENR-$CaCO_3$ compound at 30phr filler loading of $CaCO_3$

Figures 1 and 2 showed the FTIR spectra of ENR and ENR-$CaC0_3$ compounds. Both spectras showed strong peaks at 3037, 2959, and 2918cm-1corresponding to 0H, CH and C-C vibrations respectively. Also, the presence of the doublet peaks in 872 and 834 cm-1also confirmed that successful epoxidation has been achieved, these peaks are the absorbance band of C-O bond present the epoxidized natural rubber. Calcium Carbonates: containing two ions calcium and carbonate were simple in different calcium carbonate structures could be discriminated by IR spectra. The absorption bands of carbonate ion are divided into four areas

V1-(symmetric stretching) at 1080cm^{-1}, V2-(out of plane bending) at 870cm-1,V3- (double degenerates planer asymmetric stretching) at 1400cm-1 and V4-(doubly degenerate planar bending) at 700cm-1 ENR-$CaC0_3$ spectra showed presence of elastic which is evidence in the absorbance band of 711, 741 and 2522cm^{-1} these values compare with published IR data produced by FTIR of KBr pellets of 1420cm^{-1} (V3), 876cm^{-1} (V2) and 714cm^{-1}(V4) for calcite as reported by " Leong, Lee et al (2002).While for vaterite, 1090cm^{-1} (V1), 878/850cm^{-1} (V2) and 747/741cm^{1} for calcite and 741 /1036cm-1 for vaterite. Therefore, according to these results, it can be concluded that the dominate phase of all the ENR-$CaC0_3$ compound is the vaterite.

Adhesion Properties T-Peel Test

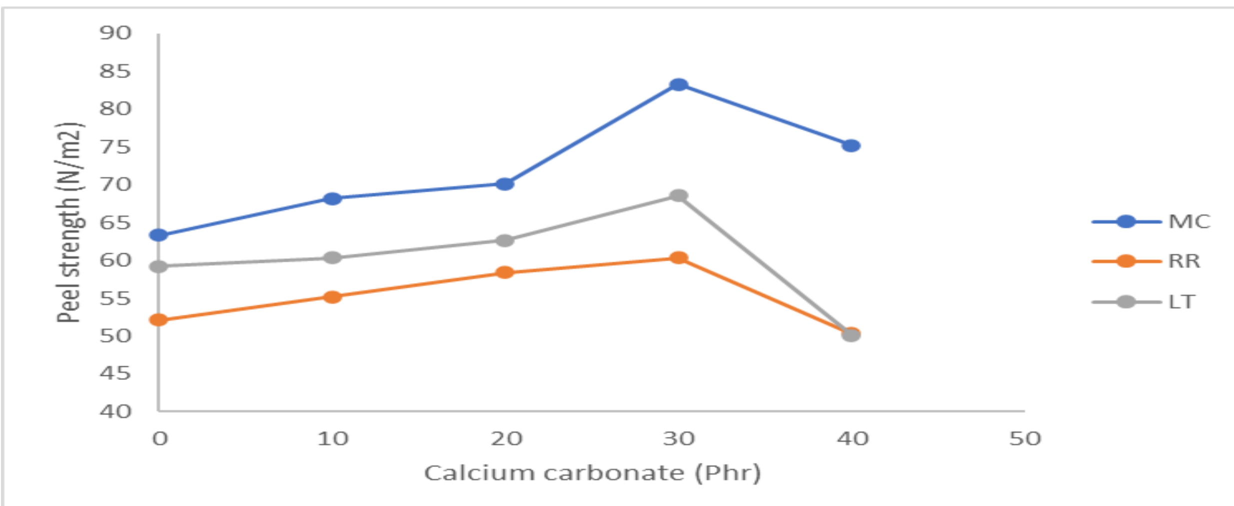

Figure 3: Peel strength of ENR-CaCO3 Adhesives on Microcellular (MC), Resin rubber (RR) and leather (LT) outsoles

The dependence of Peel strength on $CaCO_3$ loading using T-Peel is shown in figure 3. From the results obtained, it indicates that the peel strength initially increased at 10phr to 30phr loading of $CaCO_3$ with the maximum peel value of 82.1 N/m^2.This phenomenon is explained by the occurrence of maximum wettability as $CaCO_3$ concentration is increased. The increased in wettability is followed by increase in mechanical interlocking and anchorage of the adhesive in pores and irregularities in the adherents as reported by Yul *et al.* (2003).

Peel strength however, decreases gradually from 30-40phr. This phenomenon is attributed to the decrease in elastic component of the adhesive resulting from the decrease of ENR-25 as the filler is increased (Poh, & Firdaus, 2011). The decrease in peel strength could also be attributed to the nature of the adherends used i.e. (resin rubber soles), and leather (LT) outsoles used.

Lap Shear Test

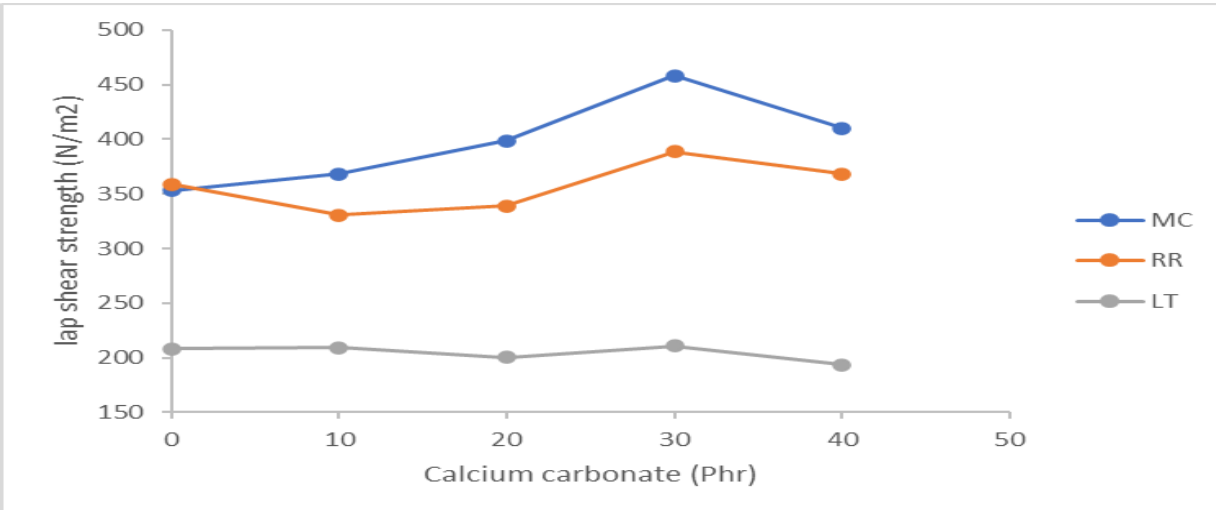

Figure 4: Lap shear test ENR-CaCO3 adhesive on microcellular (MC), Resin rubber (RR), and leather (LT) outsoles

Figure 4 shows the lap shear test of ENR-$CaCO_3$ adhesive on MC, RR and LT out soles. From the results obtained, there was a rapid increase in lap shear test at 10phr of $CaCO_3$, after which a slight drop of lap shear strength increase in filler loading was observed. The rapid increase in lap shear strength could be attributed to the high compatibility between the ENR-25 which is polar and the microcellular (MC) out sole which is a non-polar adherend. Also, the slight decrease at 20phr of $CaCO_3$, is attributed to the decrease in cohesive strength of the adhesive.

The shearing effect is higher in the presence of $CaCO_3$ this is because of the smoothness nature of the surface of the microcellular sole which consequently resulted in the increase in the shearing resistance of the adhesive on the substrate (Poh & Saari., 2011). Maximum value was observed at 458N/m^2 of lap shear strength at highest concentration of 30phr of $CaCO_3$, further addition of $CaCO_3$ from 30-40phr decreased the lap shear strength, this is due to the increased wettability of the $CaCO_3$ as its concentration was increased, which reduced the shearing resistance of the adhesives, leading to a slight drop in the lap shear strength at 40phr loading of the filler.

Effect of Temperature on the Lap Shear Strength of ENR-$CaCO_3$ Adhesives

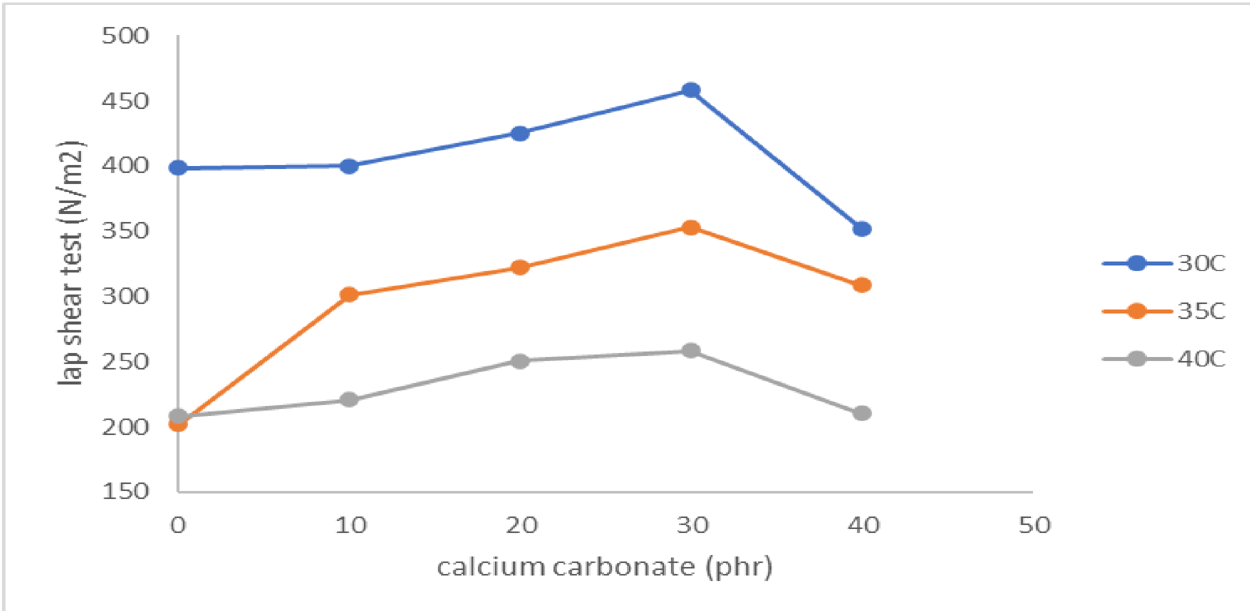

Figure 5: Effect of temperature on the lap shear strength of ENR-CaCO3 adhesives on micro cellular outsoles

Figure 5 above shows the effect of temperature on the lap shear test of ENR-$CaCO_3$ adhesives at 30°C, 35°C, and 40°C, on microcellular (MC) outsoles. From the results obtained it can be seen that the temperature had a slight effect on the lap shear of the adhesive at 35°C, and 40°C respectively, for the control sample which had no filler, the addition of $CaCO_3$ showed gradual increase initially at 10-20phr, but decreases with a further addition of the filler from 30phr as the temperature increases. At 40°C increase in temperature a rapid decrease was observed at 10phr followed by a gradual increase from 20-30 phr as the filler loading of $CaCO_3$ was increased.

Therefore, at 30°C using microcellular outsole gave the best result as the optimum lap shear was seen at 458.3N/m^2 (Poh & Kwo, 2007).

Effect of Temperature on the Peel Strength of ENR-CaCO3 Adhesives

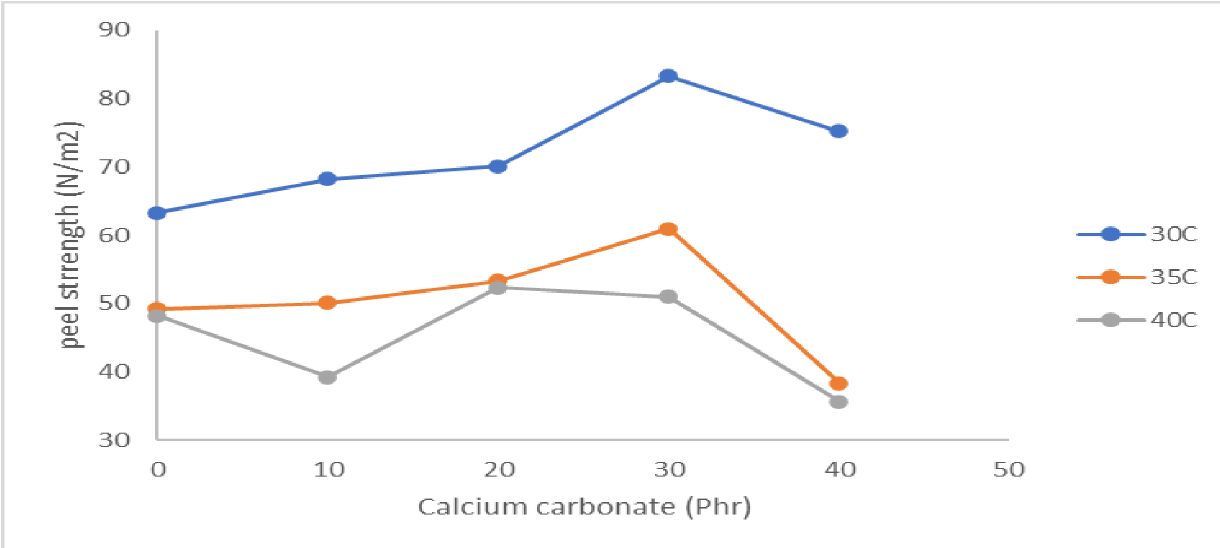

Figure 6: Effect of temperature on the peel strength of ENR –$CaCO_3$ adhesives at $30^{O}C$ $35^{O}C$& $40^{0}C$ on micro-cellular (MC) outsoles

Figure 6 shows the effect of temperature on peel strength of ENR-$CaCO_3$ at $30^{0}C$, $35^{0}C$, $40^{0}C$ on Microcellular (MC), resin rubber (RR) and leather (LT) outsoles respectively. From the results obtained, was observed that the temperature had a considerable effect on the peel strength of the adhesive at 40°C especially for the control sample which had no filler the addition of $CaCO_3$ showed gradual increased initially at 10-20phr but decrease with a further addition of the filler from 30phr at 40°C increase in temperature a rapid decrease was observed at 10phr followed by a gradual increase from 20-40phr as the filler loading of $CaCO_3$ was increase. Therefore, at 30°C using microcellular (MC) outsole sole, gave the best result and the optimum peel strength was seen at 83.3N/m^2.

Viscosity Test Viscosity 10^3(Cp)

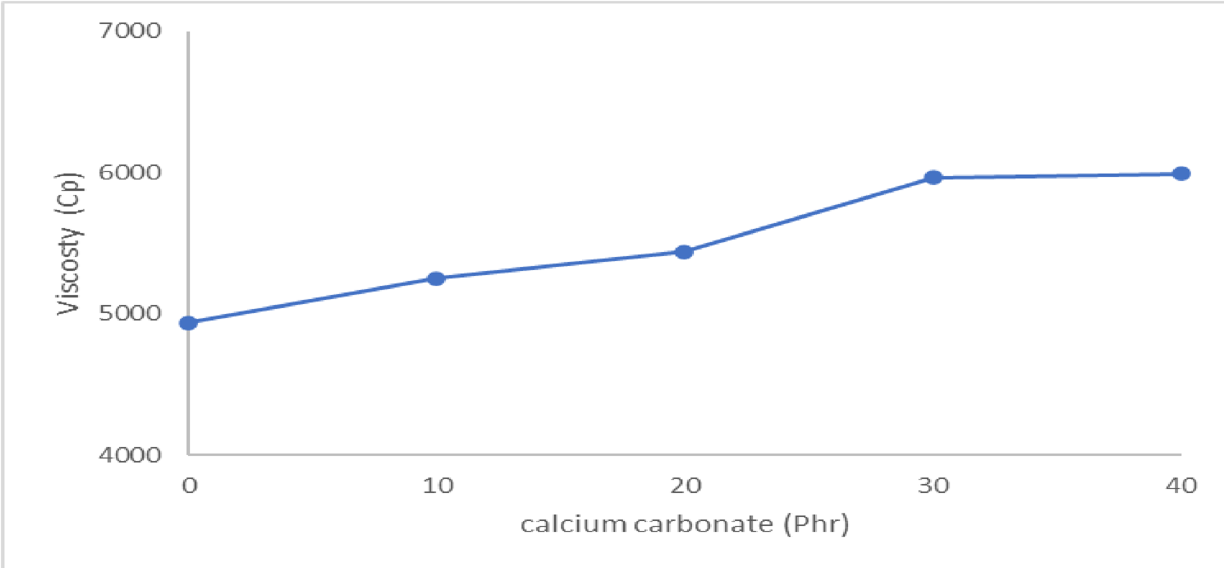

Figure 7: Viscosity of ENR-$CaCO_3$ adhesives.

Figure 7 shows the viscosity of the ENR-$CaCO_3$ adhesives at different filler loadings. The result obtained, shows the dependence of viscosity of the adhesives on calcium carbonate concentration. The viscosity of the adhesives increases gradually initially, followed by a slight decrease between 20-30phr of CaCO3.But increases gradually at 40phr which is the highest concentration of the $CaCO_3$.

This observation is attributed to the increasing thickening effect of the $CaCO_3$ which acts as filler in the adhesive. However, at 30phr calcium carbonate loading the thickening effect stabilizes as reflected by the gradual increase in viscosity with further addition of the $CaCO_3$. ENR25 is a chemically modified natural rubber which contains 25% of epoxidation of the $CaCO_3$ gives rise to molecular interaction between the filler and ENR-25, thus giving rise to higher viscosity of adhesive.

Chemical Resistance

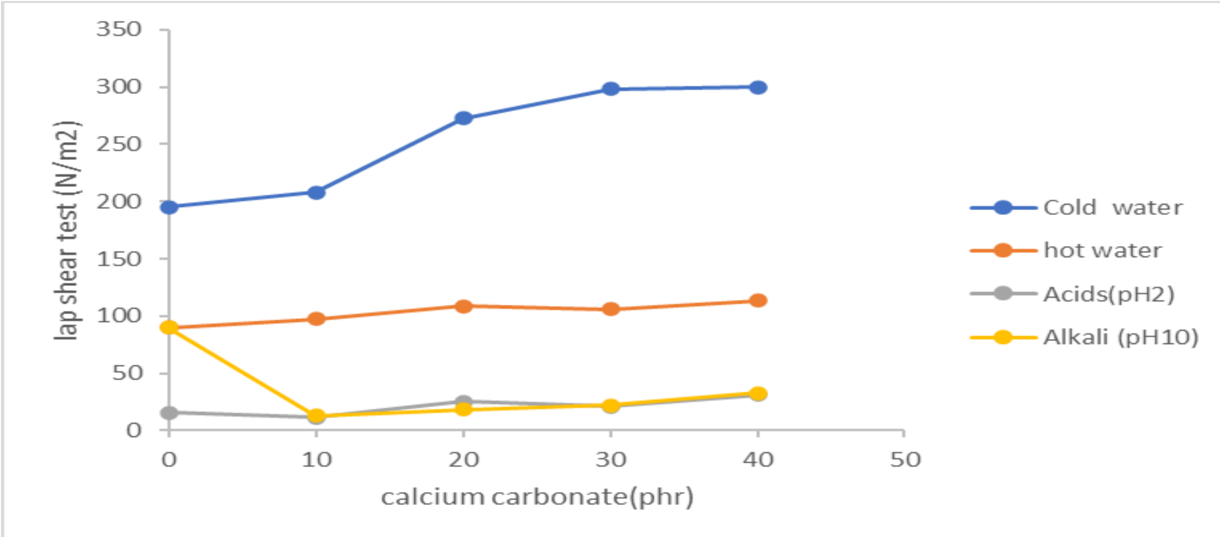

Figure 8: Effect of chemicals on the lap shear test of ENR-$CaCO_3$ adhesives on Microcellular outsoles

Figure 8 showed the chemical resistance of the ENR-CaCO3adhesives on MC outsoles. The adhesive showed good resistance to cold and hot water as the filler loading increases from10-40phr filler loading, acids decreased adhesive performance to some extent while the alkali has the most detrimental effect on the adhesive performance.

CONCLUSION

Based on the study, the following conclusions were drawn:

1. The work has shown that epoxidized natural rubber (ENR-25) filled calcium carbonate pressure sensitive adhesives was successfully prepared. The characterization of the adhesives using FTIR spectroscopy, revealed important peaks which confirmed the presence of C-O and $CaCO_3$ bonds due to epoxidation in both the ENR-25 and ENR$CaCO_3$ compounds.
2. The adhesives showed initial increase at 10phr loading $CaCO_3$ with maximum peel value at 82.1 N/m^2 peel strength value and decreases gradually with increase in $CaCO_3$ loading from 30-40phr, due to increase in wettability effect as the filler loading was increased in all the substrates.

3. The microcellular out soles showed the best adhesion properties in terms of lap shear test and peel strength of the adhesive bonds. The effect of temperature on the lap shear test of adhesives on MC out soles only showed a slight decrease at 35ºC and a significant decrease at 40ºC, on all the adhesives.
4. The chemical resistance of adhesive on the peel strength and lap shear strength had a good resistance to cold and hot water, moderate resistance to and weak resistance to alkalis on the MC sole.

REFERENCES

Ebnesajjad, S. (2011). History of adhesives." *Handbook of Adhesives and Surface Preparation: Technology, Applications and Manufacturing. Amsterdam Elsevier*. ISBN 978143774461, 137.

Hashim, A. S., & Ong, S. K. (2014). Application of epoxidized natural rubber (NR) in pressure sen- sitive adhesives (PSAs). In S. Kohjiya and Y. Ikeda (eds), *Chemistry, manufacture and application of natural rubber* (353-370). United Kingdom: Elsevier Woodhead Publishing.

Poh, B. T., & Firdaus S. Z. (2011). Viscosity, shear strength, and peel strength of polyethylene terepthalate of natural rubber-based adhesives containing hybrid tackifiers. *Journal of Vinyl and Additive Technology, 17*(3), 209-212. https://doi.org/10.1002/vnl.20273.

Poh, B. T. (2007). Adhesion properties of styrene-butadiene rubber (SBR) standard Malaysian Rubber (SMR) based adhesive in the presence of phenol formaldhehyde resin. *Express polymer letters, 1*, 654-659. https://doi.org/10.1002/app.26072.

Poh, B. T., & Saari, N. (2011). Adhesion properties of epoxidized natural rubber-based adhesives in the presence of magnesium oxide. *Journal of Elastimers and Plastics, 43*(4), 357-368. DOI: 10.1177/0095244311404185.

Poh, B. T., & Kwo, K. H. (2007). Peel and shear strength of pressure sensitive adhesives prepared from epoxidized natural rubber. *Journal of Applied Polymer Science, 105*(2), 680-684.

Poh, B. T., Lee, P. G., & Chuach, S. C. (2008). Adhesion property of epoxided natural rubber (ENR-25 and ENR-50) filled with calcium carbonate. *Express Polymer Letters, 2*(6), 398403. DOI: 10.3144/expresspolymlett.2008.48.

Sandip, D. D., Jigar, V. P., & Vijay, K. S. (2003). Polyurathane adhesives system from biomaterialbased polyol for wood bonding. *International Journal of Adhesion and Adhesives, 23*(5), 393-399.

Shrikant, A. (2018). *Inclusion of adhesive as new subject Syallabusn in printing technology*. Pune Maharashtra, India: Collage of engineering and technology.

Yul, C. L., Larry, M. S. L., & Seng, N. G. (2003). The viscoelastic of natural rubber pressure sensitive adhesive using acrylic resin as tackifer. *Journal of Applied Polymer Science, 8*, 2118-2123.