Leather-Like Material Based on Natural Rubber Composites

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ABSTRACT: *In-house leather like material based on filled natural rubber (NR) with various filler types (i.e., clay, SiO_2 and $CaCO_3$) was prepared by calendaring method. NR/SiO_2 exhibited the highest tensile strength, 100% modulus, elongation at break, and tear strength. The lower wear index and % weight loss in case of NR/SiO_2 indicated the best abrasion resistance among the other fillers due to the fine dispersion of SiO_2 in the NR matrix. Also, the uniform dispersion of SiO_2 together with high surface area of SiO_2 enhanced the interaction with NR matrix led to the higher elasticity of NR/SiO_2 vulcanisate. Therefore, NR/SiO_2-based leather was prepared and exhibited no significant difference in the abrasion resistance compared to the commercial leather. Furthermore, it was observed that NR/SiO_2-based leather exhibited higher skid resistance than the commercial one. Therefore, NR/SiO_2-based leather has been proposed to use as commercial artificial leather.*

Keywords: natural rubber, leather-like material, abrasion resistance, filler
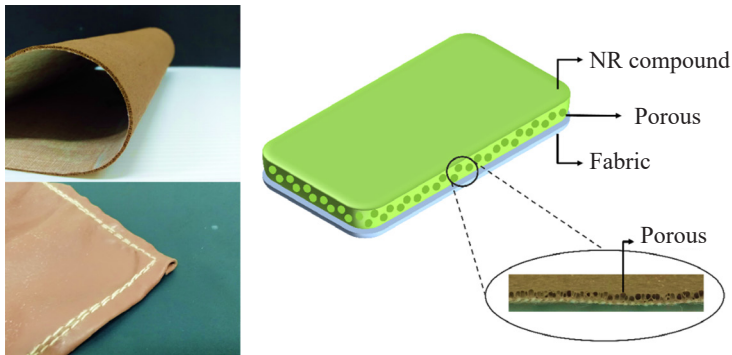
Morphological structure models of NR based leather-like material

1.   INTRODUCTION

Artificial leather is an alternative material for leather used in several products including briefcases, stationery items, garments, belts, sports items footwear, etc. Artificial leather industry plays a major role on developing the economy in terms of export earnings and employment opportunities.[1]

In general, leather has been prepared by impregnating a nonwoven fabric/ knitted goods with a polyurethane (PU) dissolved in an organic solvent using dimethylformamide (DMF), and also PU with microfiber polycaprolactam (PCL) in the presence of DMF and formic acid.[2,3] Such type of leather exhibits sufficient properties due to the excellent abrasion resistance, flexibility, durability, and toughness of original PU matrix. Polyvinylchlorides (PVC) can be used as a leathered matrix, which shows superior thermal releasing properties.[4] However, it was reported that PU and PVC based leathers have chemical contamination which attacks the environment due to the tremendous harmful solvents used during the preparation and adhesion processes.[5] Attempts have been made to replace or minimise the use of toxic chemicals and the leather–like composites based on natural rubber (NR) is introduced.

As a biosynthesised polymer with high elasticity, flexibility and abrasion resistance, NR is suitable for leather materials. It was reported that, the properties of NR can be varied by the addition of fillers, such as silica (SiO_2), clay and calcium carbonate ($CaCO_3$). This causes effectively to increase the mechanical properties of NR by incorporating fillers at different concentrations.[6–8] The major change occurs not only in case of sheet form, but also in the form of NR foam which performs well by using blowing agent. This generates an open-cell structure of NR matrix owing to the release of carbon dioxide gas at

approximately 150°C.[6] However, it was reported that the blowing mechanism interrupted effectively the crosslink density of NR and the mechanical properties.[7] The cell size of the foam can be adjusted by varying the concentration of the gases. It was also noted that, increasing the blowing agent leads to rise the gas decomposition, reduces the average cell size, and increases the number of cells.[7]

Therefore, the present work is aimed to study the suitable rubber formulation for preparing NR based leather-like material with various fillers (i.e., clay, SiO_2 and $CaCO_3$). The NR compound was fabricated by following the textile calendaring procedures in order to evaluate the optimised strength of leather. In addition, mechanical properties, cure characteristic together with morphologies were examined. Also, leather-like material based on NR from a proper NR formulation was developed and compared with the commercial leathers, i.e., PVC and PU-based leathers in terms of abrasion resistance, skid, and puncture resistances.

2.   EXPERIMENTAL

2.1   Material

NR (Standard Thai Rubber 5L grade) with density 0.92 g/cm^{3} was manufactured by Chalong Latex Industry Co. Ltd. Songkhla, Thailand. Other chemicals used in the rubber formulation such as zinc oxide (ZnO), stearic acid, $CaCO_3$, china clay, SiO_2, sulphur, tetramethyl thiuram disulphide (TMTD), and 2-2'-Dithiobis (benzothiazole) (MBTS, were purchased from Lanxess Co. Ltd., Bangkok, Thailand. The blowing agent, Dinitrosopentamethylene tetramine (DPT) was purchased from Kij Paiboon Chemical Ltd., Bangkok, Thailand.

2.2   Preparation of Natural Rubber Compound

Table 1: Formulation of NR vulcanisates.

Ingredients	(phr)*
STR5L	100
ZnO	5
Stearic acid	1
TMTD	1
MBTS	1
DPT	5
Fillers ($CaCO_3$, Clay and Silica)	30
Sulphur	3

*Note: *Part per hundred parts of rubber by weight*

NR compounds were prepared by following the formulation as shown in Table 1. The mixing was performed on an open two-roll mill at room temperature with the rotor friction ratio of 1:1.4. Initially, NR was masticated for 5 min and mixed with the activators (i.e., ZnO and stearic acid) for 2 min. Then, the fillers ($CaCO_3$, clay, or SiO_2) were added individually into the compound. Further, the blowing agent DPT was incorporated before the addition of accelerators (i.e., MBTs and TMTD) and sulphur. Compounding was continued for a total mixing time of 30 min and the cure characteristics of rubber compounds were then determined by a moving die rheometer (MDR, Alpha Technologies, USA) at 150°C. NR vulcanisates were eventually prepared using compression moulding at 150°C following the respective cure time form MDR.For the preparation of leather-coated textile vulcanisates, the compound was fabricated on textile using calendaring processes. Here, approximately 2 mm of the calendaring nip was used under the controlled rolling condition of 60°C with arolling speed of 15 rpm. Subsequently, the NR leather-coated textile was then heated in a hot air oven at 150°C for controlled time as performed in the case of un-coated samples.

2.3   Characterisation

2.3.1   Cure characteristics

The cure characteristics of gum NR and its compounds filled with $CaCO_3$, clay and SiO_2 were investigated using a MDR (Alpha Technologies, USA) according to ASTM D224. In each case, the sample was tested by fixing the oscillation frequency of 1.66 Hz and 1 arc amplitude at 150°C for 20 min.

2.3.2   Mechanical properties

Mechanical properties were investigated using an Instron machine (Model 3365) according to ASTM D412. The specimens were cut into dumbbell shapes and the test was conducted through a 1000 N load cell at a cross head speed of 500 mm/min^{-1}. The tear strength was estimated following ASTM D624 using unnicked 90° angle test pieces. The crosshead speed used was 500 mm/min^{-1}. Hardness testing was performed using a Shore A durometer (Frank GmbH, Hamburg, Germany), according to ASTM D2240.

2.3.3 Abrasion resistance

The abrasion resistance of the samples was studied with a Taber abraser following ASTM D4060-10. Thus, wear index (I) is realised to be abrasion ability relating to the observed % weight loss (L) of the samples, as seen in Equation (1)–(2):

$$I = \frac{(A - B)1000}{C} \tag{1}$$

$$\text{Weight loss (L)} = \frac{A - B}{A} \times 100 \tag{2}$$

where: A = weight of test specimen before abrasion (g)
B = weight of test specimen after abrasion (g)
C = number of cycles of abrasion recorded

2.3.4 Puncture resistance

Puncture test was carried out on tensile testing machine Z005 (Zwick Roell, Germany). The puncture probe was held by a pin chuck mounted on the load cell. NR vulcanisate was clamped between two steel plates under air pressure. The hole in lower plate was chamfered to avoid stress concentration under 100 mm/min of probe speed.

2.3.5 Skid resistance

In-house leather based on NR, real leather, PVC, and PU were tested using skid resistance from a British pendulum skid tester (BPST) (S885, Wessex, United Kingdom), at 25°C. This value was essentially measured by means of the energy loss of rubber pad sliding over a flat surface.

2.3.6 Morphologies

Microstructural characterisation of gum NR and its vulcanisates filled with $CaCO_3$, clay, and SiO_2 at the loading level of 30 phr were investigated using optical microscope (Phenom Prox Scanning Electron Microscope, Brno, Czech Republic) at accelerated voltage of 15 kv, 80 μm resolution and x1000 magnification. In order to evaluate the dispersion of fillers in NR matrix, scanning electron microscope (SEM, model JEOL JSM-5800LV, Tokyo, Japan) was also employed. Specimens were cryogenically fractured in liquid nitrogen to create a fresh cross-sectional surface. Consequently, the samples were sputter-coated with a thin layer of gold under vacuum before scanning.

3. RESULTS AND DISCUSSION

3.1 Specific Properties of Leather-Like NR Product
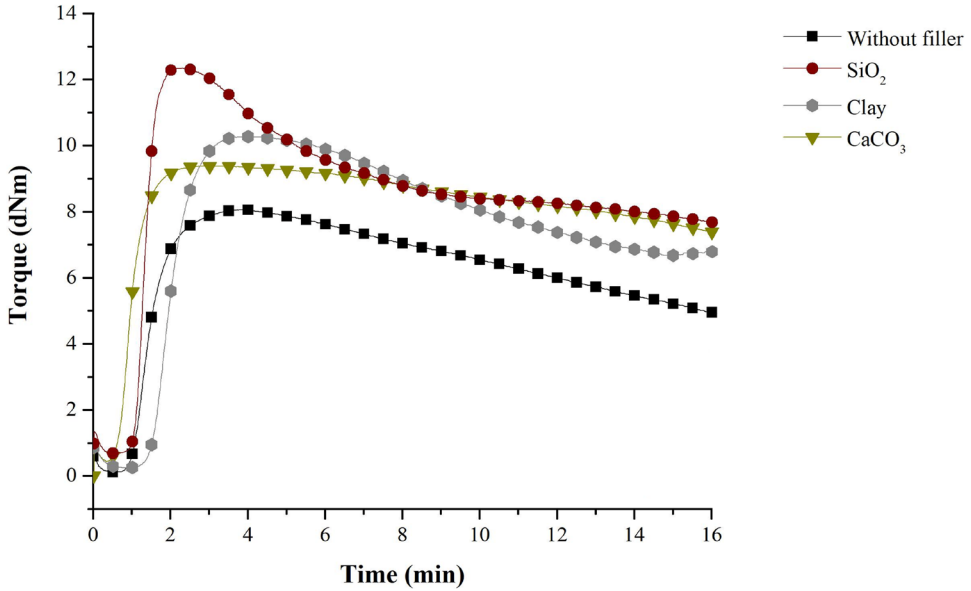
3.1.1 Cure characteristics

Figure 1: Curing curves of gum NR (without filler), SiO_2, clay and $CaCO_3$ filled NR compounds.

Figure 1 shows the cure characteristic curves of gum NR (without filler) and the compounds filled with SiO_2, clay and $CaCO_3$. Also, Table 2 summarises the respective curing characteristics of the samples in terms of scorch time (t_{s2}), cure time (t_{90}) and torque difference (M_H-M_L). All the compounds showed reversion phenomena due to thermo-oxidative degradation of weak linkages based on the existed polysulfidic –S-S– bonds.[8] Here, the NR/SiO_2 compound exhibits the largest reversion degree due to the breakage of silica agglomeration. The strong hydroxyl polarity of SiO_2 particles develops high tendency of filler-filler interaction in the NR matrix rather than filler-rubber attraction.[9] Considering t_{s2} and t_{90} values, clay exhibited an increasing trend due to the china clay forms zinc silicate with ZnO. These reactions may reduce the efficiency of ZnO in curing system which slowly resulted in the occurrence of vulcanisation reaction.[10] Meanwhile, the values of Tc_{90} in case of SiO_2 and $CaCO_3$ filled NR compounds are found to be decreased, might be due to the effect of moisture-treated silanol groups on the SiO_2 surfaces

accelerate crosslinking.[11] In addition, the interaction between NR with SiO_2 caused to reduce retarding reaction between silica and zinc oxide accelerator. Moreover, $CaCO_3$ filled NR compound shorten the Tc_{90} value due to the fact that $CaCO_3$ particles are isotropic in nature which leads to an increased thermal conductivity of NR matrix, consequently, faster vulcanisation has been observed.[12]

Table 2: Cure characteristic of gum NR (without filler) SiO_2, clay and $CaCO_3$ filler NR compounds.

Sample	M_H (dNm)	M_L (dNm)	M_H- M_L (dNm)	T_{s2} (min)	T_{C90} (min)
Without filler	0.11	8.05	7.94	0.90	2.23
$CaCO_3$	0.44	9.38	8.94	0.52	1.50
Clay	0.24	10.27	10.03	1.30	2.62
SiO_2	0.68	12.34	11.66	0.96	1.62

Note: M_L = Minimum torque, M_H = maximum torque, M_H-M_L = torque difference, Ts_2 = scorch time, and Tc_{90} = cure time

This means that the clay retards vulcanisation of NR, whereas SiO_2 and $CaCO_3$ accelerate the curing reaction and vulcanises earlier. The result effectively affects the generation of crosslinking among NR molecules. It clearly clarifies from the M_H-M_L values, which are directly related to the degree of chemical linkages originating in the matrix.[13] In Table 2, it is clearly seen that the NR/SiO_2 showed the highest M_H-M_L value, even though it has a strong reversion behaviour. This can be explained by the characteristics of SiO_2 which is having a small particle size with strong polarity compared to clay and $CaCO_3$. In the NR matrix, SiO_2 forms strong agglomeration but also generates high bound rubber absorption owing to it surface area. It means that, SiO_2 can reinforce well in the NR matrix and provides higher crosslink density. On the other hand, the M_H-M_L values of NR/clay and NR/$CaCO_3$ exhibited higher values than the pure NR, and still lower than the case of NR/SiO_2. This can be examined by the specific structure of the filler. According to the layered structure of clay, a strong agglomeration may also occur, whereas the smooth surface of clay due to the packing of aluminium silicate found difficult in the rubber absorption on its surface. This lowers the bound rubber absorption, which is the reinforcement mechanism of filler inside the rubber matrix, indicating poor M_H-M_L. However, the addition of $CaCO_3$ into NR lowers the value of M_H-M_L. It was reported that, the smaller particle size with larger surface area leads to enhance the interaction between filler and rubber matrix.[14] Therefore, the large particle size of $CaCO_3$ provided low specific surface area of filler lead to poor interaction between $CaCO_3$ and rubber matrix, hence it shows lower rubber absorption on the $CaCO_3$ surface.
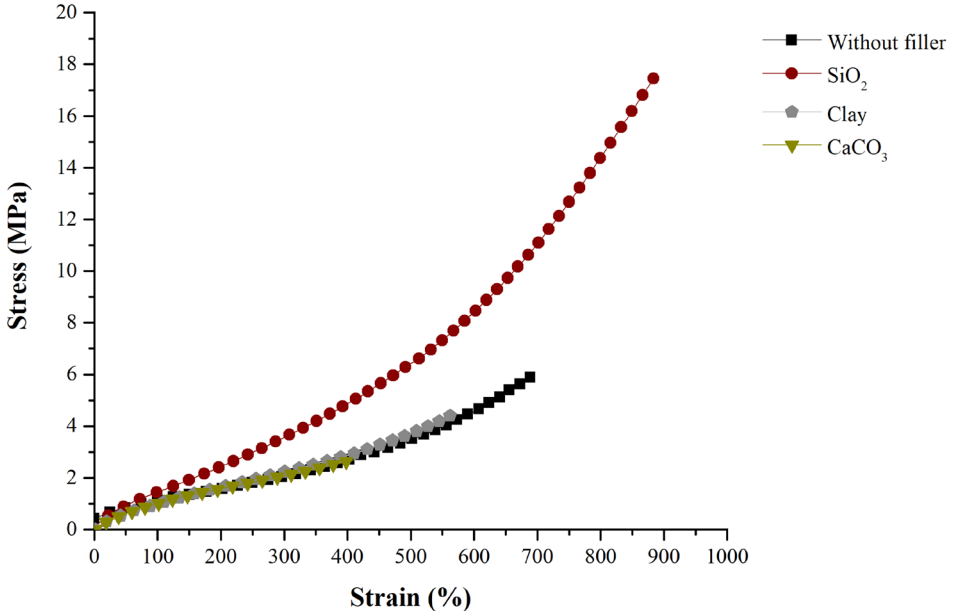
3.1.2   Mechanical properties

Figure 2:   Stress-strain curves of in-house leather based on NR vulcanisate for different fillers; gum NR (without filler), CaCO$_3$, clay, and SiO$_2$.

Figure 2 shows the stress-strain curves of the in-house leather based on NR vulcanisates filled with CaCO$_3$, clay and SiO$_2$ fillers. The details of modulus at 100% elongation, tensile strength, and elongation at break from the stress-strain plots together with tear strength and hardness are summarised in Table 3.

Table 3:   Mechanical properties in terms of 100% modulus, tensile strength, elongation at break, tear strength and hardness of in-house leather based on NR vulcanisate with CaCO$_3$, clay and SiO$_2$ particulates.

Sample	100% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (N/mm)	Hardness (Shore A)
Without filler	1.12±0.01	5.98±1.61	685.00±81.33	27.73±0.46	40±1.00
CaCO$_3$	0.98±0.03	2.67±0.41	413.21±72.09	21.20±1.72	41±1.00
Clay	0.98±0.01	4.38±0.15	569.75±08.14	22.05±1.74	43±0.57
SiO$_2$	1.40±0.05	17.54±1.06	897.46±21.04	35.82±0.78	52±1.52

In Figure 3, it is clearly seen that the addition of clay and $CaCO_3$ in the NR matrix reduces the modulus, tensile strength, and elongation at break of the vulcanisates compared to the gum NR. This correlates well with the observed values of crosslink density calculated from M_H-M_L. It indicates that the large particle size of clay and $CaCO_3$ causes poor rubber absorption on the filler surfaces reduces the reinforcement efficiency and it reflects in the weak mechanical properties. On the other hand, the highest properties are observed in case of NR/SiO_2 vulcanisates due to the better reinforcement. Here, existence of SiO_2 particles effectively causes the physical absorption of rubber within the glassy levels. This restricts the deformation of NR matrix under an applied force and therefore the breakages of NR chains have been retarded. This can be explained by the proposed model as shown in Figure 3. It is clearly seen that; all the fillers have significant shape and particle size differences. $CaCO_3$ and clay exhibited the larger particle sizes than that of SiO_2. It clarifies the reason to achieve the highest mechanical properties than the other fillers (Figures 3(A) – (D)). Higher value of elongation at break is noticed in case of NR/SiO_2 than that of NR/clay and NR/$CaCO_3$. This might be due to the fine dispersion of SiO_2 together with the higher surface area of SiO_2 supported better interaction with NR matrix enhanced the elasticity of NR/SiO_2 vulcanisate.
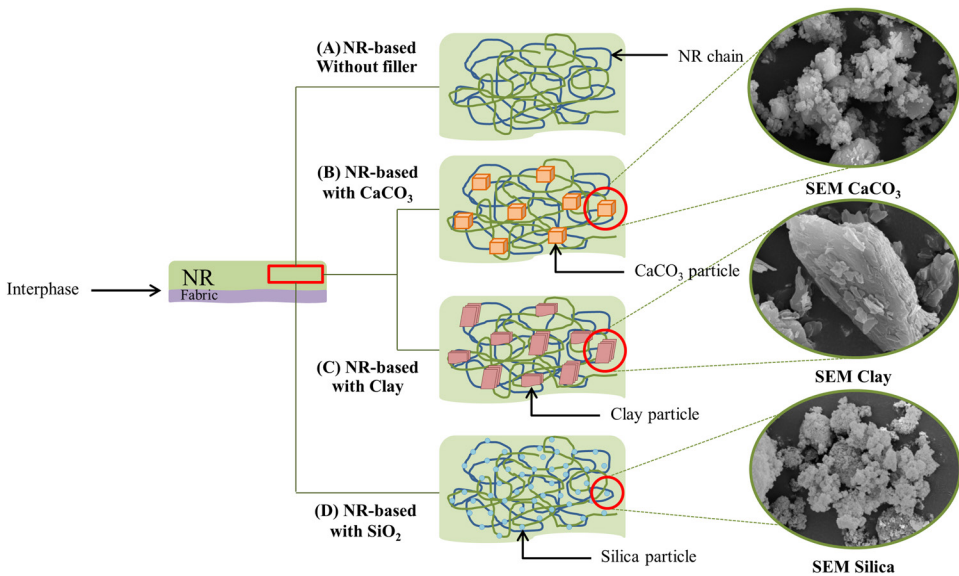
Figure 3: Proposed model of $CaCO_3$, clay and SiO_2 filled NR vulcanisate for in-house leather.

On the other hand, larger particles of $CaCO_3$ and clay resulted in poor dispersion and consequently agglomeration occurs, which becomes the weak point in the matrix. Variation of tear strength and hardness of the samples are as shown in Figure 4 and Table 3. Similar behaviour is observed in the tear strength and hardness as seen in the tensile properties. Higher tear strength and hardness are also achieved in the NR/SiO_2 vulcanisate due to the small particle size of the filler, which affects effectively the reinforcement efficiency in the NR matrix. The filler-rubber interaction can also be extrapolated with the cracking extension of the samples under the applied force. With the highest value of tear strength, it is seen in the glassy bound rubber, attraction between the rubber molecules, and SiO_2 surfaces retards significantly the crack propagation of the NR phases during the breakage of samples.

3.2   Durability of NR-based Leather
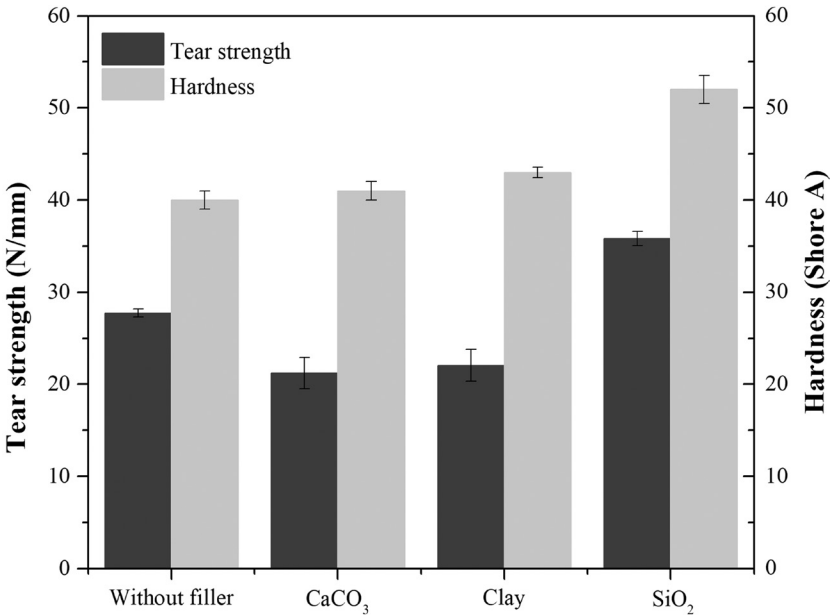
Figure 4:   Tear strength and hardness of in-house leather based on NR vulcanisate with various fillers.

Durability of leather in terms of tear resistance, hardness, and the abrasion ability together with puncture force and skid resistance are examined. Figure 4 displays tear strength and hardness of the leather filled with $CaCO_3$, clay, and SiO_2. It is seen that the addition of SiO_2 has significantly affected on both the properties as noticed in the mechanical properties (Figure 2). The physical

absorption of NR molecules onto the SiO_2 surfaces effectively reduces the crack propagation of NR matrix during extension. It can also be clarified by the significant increase in tear strength of the vulcanisates reinforced using SiO_2 when compared to the other fillers as shown in Figure 4.

It is not only affected the strength, but also strongly affected the abrasion resistance. Figure 5 shows the wear index and %weigh loss of the vulcanisates. An increase in the hardness of vulcanisates along with abrasion resistance is also observed. It leads the NR/SiO_2 with low wear index than the ones filled with $CaCO_3$ and clay. This can be correlated to the observed tensile and tear strengths. Addition of SiO_2 in the NR matrix provided higher degree of filler-rubber interaction due to its smaller particle size and higher surface area than those of $CaCO_3$ and clay. It clearly reflects on the abrasion surfaces of the vulcanisates as displayed in Table 4. It is clearly noted that the NR-based leather filled with $CaCO_3$ exhibited higher roughness upon damaging the leather's surface.
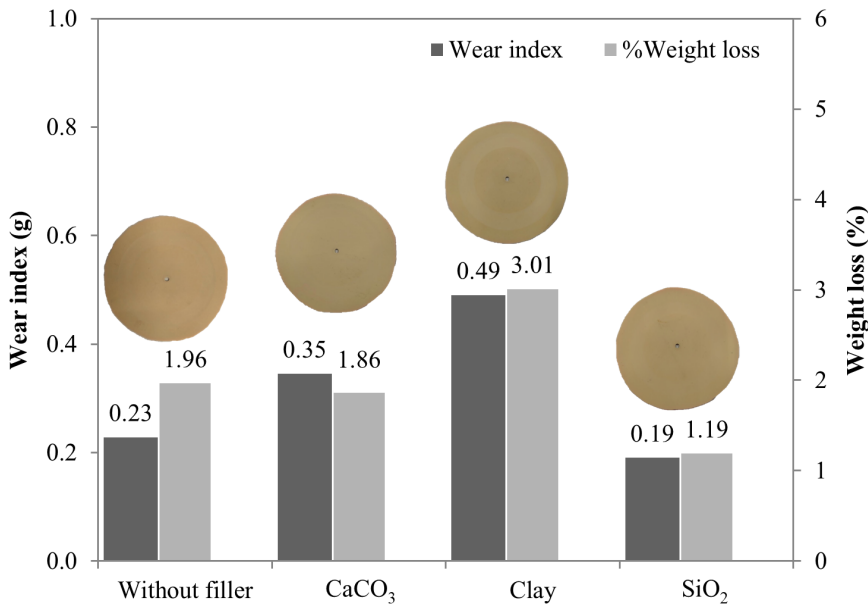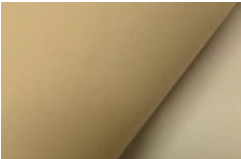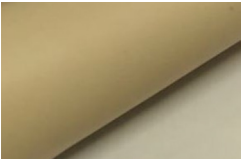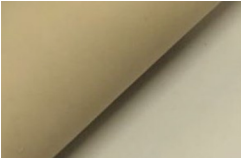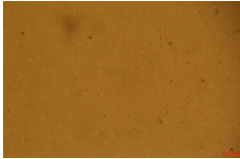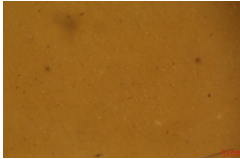

Figure 5: Abrasion resistance of in-house leather with different fillers.

The phenomenon has not been distinctly demonstrated for the vulcanisates with clay and SiO_2 responding to the observed wear ability. In addition, this is in good agreement with the measured puncture strength of the material as seen in Figure 6 and Table 4. It is observed that the in-house NR/$CaCO_3$ and

NR/clay leathers have a slight decrease in the puncture force compared to the gum NR. As expected, the NR/SiO$_2$ leather showed an enhancement in the puncture force compared to the others. This is due to the higher surface area of SiO$_2$ by attracting the NR molecules enhances effectively the reinforcement efficiency to the NR matrix and prevented the occurrence of breakages of the matrix during puncturing.

Table 4: Maximum puncture force, skid resistance, and physical appearance of inhouse leather with CaCO$_3$, clay, and SiO$_2$ particulates.

Sample	Maximum puncture force (N)	Skid resistance (PTV)	Physical appearance on surface	
			Before taber abrasion	After taber abrasion
Without filler	171.3	54		
CaCO$_3$	169.4	72		
Clay	156.8	66		
SiO$_2$	239.3	93		

In Table 4, the skid resistance of in-house NR leather is investigated and compared with the original NR. The incorporation of fillers increased well the skid resistance of the vulcanisates. The existence of hard particles strongly retards the breakages of rubber matrix and increases the strength of the vulcanisates. This means that the high surface area of the filler particles enhances the properties of the final product. This is the reason for increasing the skid resistance upon the addition of filler. It is also seen that the NR/SiO$_2$ showed

the highest skid resistance compared to the vulcanisates of $NR/CaCO_3$ and NR/clay. It correlates with the mechanical properties (Figure 2 and Table 3) together with tear and puncture strength (Figure 4 and Table 4) of the vulcanisates. Therefore, it can be summarised that the NR/SiO_2 vulcanisate is suitable for the preparation of in-house NR leather.

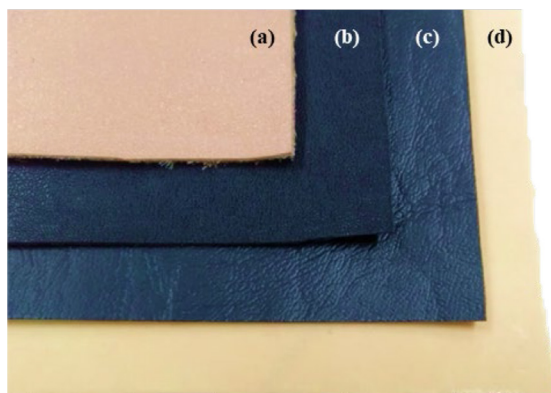### 3.3   Comparison of NR/SiO$_2$-based Leather with Commercial Products

Figure 6:   Physical appearance of (a) Real leather, (b) PU leather, (c) PVC leather and (d) In-house leather filled with SiO_2.

In order to clarify the utility of NR/SiO_2 leather, a comparison study has been done on the prepared leather with the commercial grade leather. Here, the physical appearances of real leather (Figure 6(a)), PU, and PVC leathers (Figures 6(b) and (c)) are compared with the NR based leather (Figure 6(d)). NR/SiO_2-based leather showed the smoothest surface when compared to others. This smooth surface of the sample has less attraction due to effect of polishing with stone during the measurement.

Figure 7 and Table 5 showed the lowest abrasion resistance in terms of wear index and %weight loss in case of NR/SiO_2 leather when compared to the real leather, PU, and PVC-based leathers having higher roughness. In addition, it is observed that PU leather exhibited a large increase in wear index, whereas no significant differences are observed in case of other leathers. The physical appearance after abrasion propagation and NR based leathers are comparable as seen in Figure 7. It can be seen that the surface of commercial leather exhibited high roughness while a smooth surface is observed in case of NR/SiO_2 leather. This is attributed by the suitability in terms of mechanical properties and hardness of the vulcanisates with the higher elasticity of NR matrix.
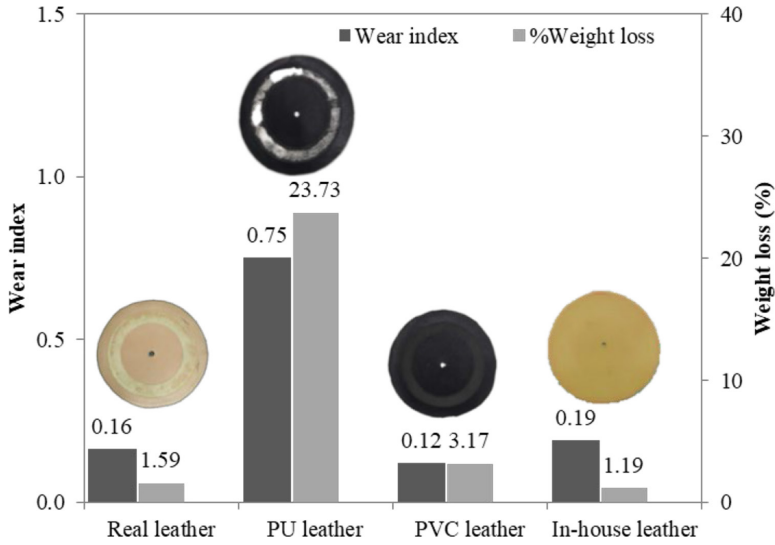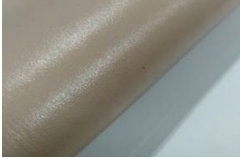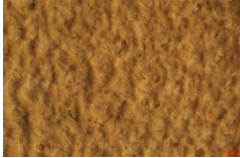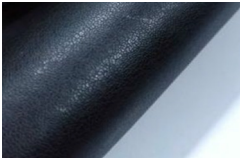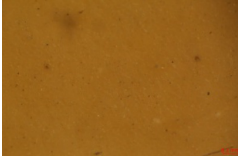
Figure 7:   Abrasion resistance of real leather, PU leather, PVC leather and In-house leather filled with SiO_2.

Table 5:   Maximum puncture force, skid resistance, and physical appearance of the in-house leather based on SiO_2 filled NR vulcanisate, real leather, PU and PVC leathers.

Sample	Maximum puncture force (N)	Skid resistance (PTV)	Physical appearance	
			Before taber abrasion	After taber abrasion
Real leather	681.0	57		
PU leather	150.1	81		

Table 5 (*Continued*)

Sample	Maximum puncture force (N)	Skid resistance (PTV)	Physical appearance	
			Before taber abrasion	After taber abrasion
PVC leather	225.6	81		
In-house leather	239.3	93		

In order to clarify the strength of the newly developed leather, puncture force, and skid resistance are examined along with the commercial leather as the reference and the results are as shown in Figure 8 and Table 5. The real leather exhibited a tremendously higher puncture force than the other artificial leathers. However, considering the artificial leather, the NR/SiO$_2$ leather showed the higher puncture force than PU and PVC-based leathers. This is due to the superior elasticity of NR together with the reinforcement efficiency of SiO$_2$ in NR matrix as highlighted in the previous section. Figure 8 and Table 5 showed the skid resistance of all leathers. It is found that the artificial leather (i.e., NR/SiO$_2$ vulcanisate, PU and PVC-based leathers) has the higher skid resistance than the real leather. Furthermore, the highest skid resistance is also obtained for the one with NR/SiO$_2$ vulcanisate. This is due to the better damping property of NR and excellent reinforcement efficiency of SiO$_2$ in the NR matrix.[15–17] Therefore, based on the observed abrasion resistance, optimal puncture force and skid resistance of the NR/SiO$_2$ leather, it can be summarised that the in-house NR/SiO$_2$ leather has the ability to use as artificial leather by replacing commercial leather.
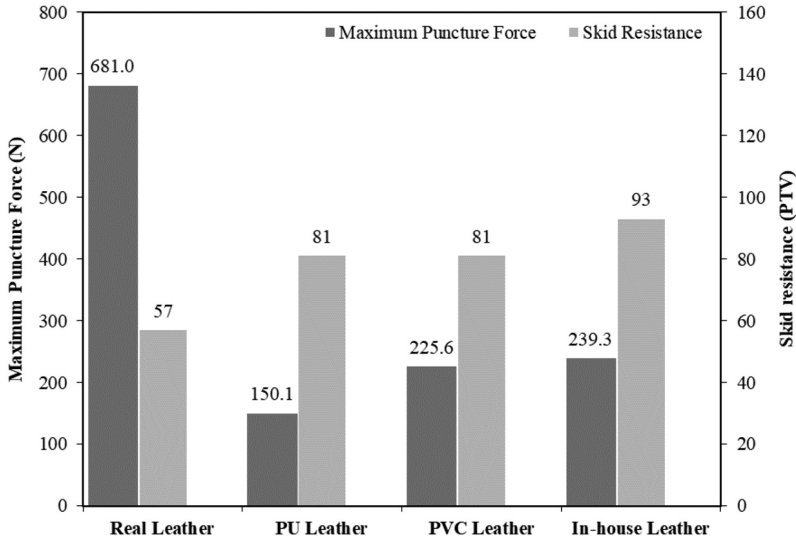
Figure 8:   Skid resistance and Maximum puncture force of real leather, PU leather, PVC leather, and In-house leather based on SiO_2 filled NR vulcanisate.

4.   CONCLUSION

Preparation of artificial leather based on NR with different types of fillers (i.e., clay, SiO_2, and $CaCO_3$) suggested that the filler type plays an important role on the properties of leather-like material in terms of particle size and their shapes. SiO_2 can reinforce well into the NR matrix and provides higher crosslink density. Therefore, NR/SiO_2 showed the higher M_H-M_L than those of NR/clay and NR/$CaCO_3$, and it depends on the specific structure of the filler. Moreover, NR/SiO_2 exhibited the highest tensile strength, 100% modulus, elongation at break, and tear strength. The existence of SiO_2 particles attracted the physical rubber absorption within the glassy levels effectively. This restricts the deformation of NR matrix under an applied force and hence the breakages of NR chain have been retarded. Durability of the leather in terms of tear resistance, hardness, and abrasion ability together with puncture force and skid resistance were showed the optimum value in the leather filled with SiO_2. This means that the physical absorption of NR molecules onto the SiO_2 surfaces effectively reduces the crack propagation of NR matrix during extension. It can be clearly confirmed from the significant increase in tear strength of the vulcanisates reinforced with SiO_2 compared to the other fillers. Furthermore, NR/SiO_2-based leather was compared to the commercially available product. It was observed that NR/SiO_2 leather showed a smoother surface than the real leather, PU and PVC

leathers. In addition, no significant difference was observed in the wear index when compared to the real leather. It indicates the applicability of NR/SiO_2-based leather as a commercial product with better abrasion resistance. In addition, NR/SiO_2-based leather exhibited lower maximum puncture force than the real leather, while it has higher maximum puncture force than PU and PVC leathers. The highest skid resistance was observed in case of NR/SiO_2-based leather. Therefore, in terms of abrasion resistance, maximum puncture force, and skid resistance, it can be confirmed that NR/SiO_2 leather is the best choice for the development of artificial leather.

5.   ACKNOWLEDGEMENTS

6.   REFERENCES

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