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SUSTAINABLE HYDROPHOBIC COATING ON PAPER BASED ON NATURAL RUBBER LATEX AND BUTYL STEARATE




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Abstract:

Sustainable hydrophobic coatings on paper have become increasingly important due to the high demand for environmentally friendly materials. In this study, a novel sustainable hydrophobic coating was developed by combining natural rubber latex (NRL) and butyl stearate (BS). The NRL acts as binder and hydrophobic agent, while the butyl stearate improves the hydrophobicity of the coating. Different coating formulations containing 0-50 wt% BS were applied to the paper using a simple bar-coating method at a constant thickness, and the hydrophobic properties were evaluated by using contact angle, Cobb and water vapour transmission rate (WVTR) measurements. The lowest WVTR value was 3.428 g/cm^2. Day, cm^2.d was obtained when NRL coated, and WVTR of 4.405 g/cm2.day was obtained with an addition of 50wt% BS, lower than the uncoated paper (5.485 g/cm^2.d.day). All the formulations promoted a remarkable decrease in water absorption (Cobb30 values decreased from 128 g/m^2 to 0.8 g/m^2, and Cobb60 values decreased from 134.4g/m2 to 0.7 g/m^2). Results showed that the coating effectively reduced the surface energy of the paper, resulting in a high contact angle of 90.6° and increased hydrophobicity. Furthermore, the NRL and butyl stearate coating demonstrated good mechanical properties, suggesting its potential as a sustainable and effective alternative to synthetic hydrophobic coatings. Overall, this study presents a promising approach for the development of sustainable hydrophobic coatings on paper, which can have significant environmental and economic benefits.

Keywords: Paper coatings, Barrier properties, Hydrophobicity, Natural rubber latex, Butyl stearate, Sustainability.

1. Introduction:

Paper is a flexible material frequently used in the food packaging sector because it is generally affordable and has good mechanical properties. Nowadays, it is gaining popularity due to growing interest in sustainable elements, including biodegradability and recyclability (Kunam et al., 2022). Paper generally consists of cellulose fibres arranged in a physical network mixed with additional additives to create a highly porous and hydrophilic composite. Being highly hydrophilic and porous paper has its uses but applications that demand barrier performance in packing face difficulties because of these characteristics (Rastogi and Samyn, 2015a)(A. Kumar et al., 2022). For application in fields like food packaging, an effective barrier to the things such as water and oxygen is very necessary (Saini et al., 2022). For paper-based packaging to satisfy the requirements for practical applications, specific treatments are required to enhance their barrier property. Surface coating is one of the most popular methods for overcoming insufficient barrier characteristics and achieving certain functionality (Li et al., 2019)(Chi et al., 2020). Currently, the paper packaging sector mainly uses synthetic polymers from fossil fuels as coating layers, leading to increasing environmental issues due to their low recyclability and lack of environmental degradability. Synthetic polymers like polyethylene, wax, carboxylated styrene-butadiene latex and polybutylene terephthalate are frequently used as surface coatings. It is important to note that the bulk of the synthetically obtained polymers described above cannot be recovered in the applications mentioned and typically contaminate land and water. About five million tonnes of plastic garbage was produced in the year 2015, which was dumped in landfills, burned in incinerators, and leaked into the environment as litter (Teixeira-Costa and Andrade, 2021). There is an increasing interest in utilizing sustainable and bio-based polymer replacements for packaging materials to substitute the present petroleum-based synthetic materials, and coatings has increased in response to this global environmental problem (Chen et al., 2019)(Rastogi and Samyn, 2015b)(Anushikha and Gaikwad, 2023).

Natural rubber (NR) is a cheap and highly available natural biopolymer that is obtained in the form of a milky white colloidal suspension from the Hevea Brasiliense rubber tree. Although around 2500 different species of plants generate NRL, Hevea Brasiliense, which is native to the river area of the Amazon, is regarded as having the highest trade value in quality and characteristics (Ramakanth et al., 2022). NR, one of the most extensively used elastomers, has a standard cis-1,4-polyisoprene structure chemically and is used in many products, including coating materials, adhesives, surgical gloves, condoms, tyres, clothes, and power transmission belts etc. (Adibi et al., 2022). NRL can be used in a wide range of applications with these advantages over synthetic rubber (Payungwong et al., 2022). Due to its outstanding film-forming capabilities, strong barrier for water, recycling abilities (Adibi et al., 2022), and flexibility, NRL may be an excellent coating choice for use in the packaging industry. While the uncured NRL can biodegrade in the soil at a slow pace, the addition of bio-fillers (such as starch, Cellulose, and chitosan) can improve the decomposition and accelerate biodegradation even more (Adibi et al., 2022). However, NRL is currently only used in a small portion of paper coatings. This is because NRL has several limitations, such as poor mechanical, oil, and weather resistance, that must be overcome to fulfil the necessary conditions to meet the demands of the paper coating market (On et al., 2012).

Butyl stearate is an ester prepared by reacting butanol with stearic acid (Pereira et al., 2018). It acts as a hydrophobic agent, which can increase the water barrier upon coating (Malakopoulos et al., 2021). As butyl stearate is a synthetic oil-based ester, it can be used as a lubricant and plasticizer. It is commonly used in personal care products as an emollient agent, plasticizer in nail paints, and masking agent in perfumes. In the food industry, butyl stearate is used as a flavouring and emulsifying agent. Its low viscosity and good lubricating properties make it sound like a lubricant for metalworking and in the production of personal care products such as lotions and creams. Butyl stearate is also used in paints and coatings.

The primary goal of this work was to investigate the development of a paper coating with strong barrier and mechanical properties while retaining environmental attributes. Additionally, it evaluates how Butyl stearate contributes to the barrier characteristics of NR formulation. In order to assess the properties of the developed paper coatings, analytical procedures such as tensile strength studies, rheology studies, water vapour transmission test, and Cobb test were used.

2. Material and Methods:

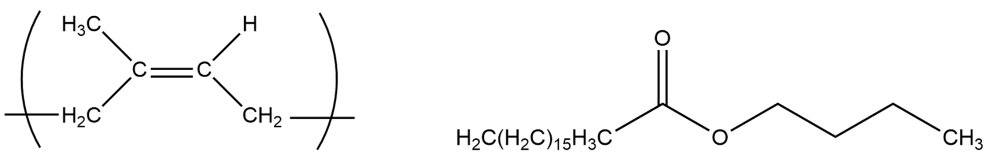
2.1 Materials:

Natural Rubber Latex (NRL) with a dry rubber content of around 60% was obtained from Japan Rubber Industries located in Mumbai (India); This obtained NRL is in milk-like white colour with a pH value equal to 10. Butyl stearate (BS), an organic fatty acid ester with 99% concentration, was obtained from the Sigma Aldrich. Cartridge paper of standard A3 size with 90 g/m^2 was obtained from the Jain Paper Merchants located in Saharanpur (India).

2.2 Coating Fabrication:

The coating formulations consist of NRL and butyl stearate. Fig 1. shows the chemical structures of the NRL and butyl stearate. The concentration of butyl stearate in the coating formulation is 10, 30, and 50% (v/v) regarding the NRL in the coating solutions, table 1. The coating solutions were intermixed with the help of a laboratory magnetic stirrer at 500rpm for 10min to achieve uniform distribution. Coating formulations are applied on the paper substrate using an automatic laboratory bar coater using a coating rod with a wire size of 50 µm. The coated papers are dried at room temperature until they are completely dried. The coater's traverse speed was held constant at 90 mm/s. Coated samples were dried in a hot air oven at room temperature for 24 hrs and named according to the amount of BS in the solutions as Neat NRL, NRL/BS10, NRL/BS30, NRL/BS50. Fig 2. illustrates the photographs of prepared coated and uncoated paper sheets showing resistance to water absorptivity.

a. b.



Natural Rubber Latex(Polyisoprene) Butyl Stearate

Fig 1. Schematic figures showing chemical structures of a) NRL (Polyisoprene) b) Butyl stearate

Table 1. Different compositions of NRL and Butyl stearate for the hydrophobic coating on the paper substrate

Sample	Natural Rubber Latex (mL)	Butyl Stearate (mL)	Total volume(mL)
Neat NRL	10	-	10
NRL/BS10	9	1	10
NRL/BS30	7	3	10
NRL/BS50	5	5	10

NRL: Natural rubber latex, BS: Butyl stearate

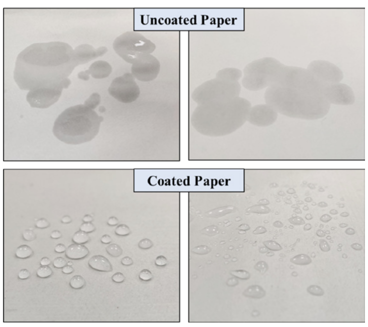


Fig 2. S Photographs of uncoated and NRL/BS-coated paper sheets showing resistance to water absorptivity

2.3 Characterization of coatings:

2.3.4 Contact Angle Measurement

To better understand the inter-molecule interactions among the coated paper sheets and deionized water, the contact angle (CA) was examined. Measuring contact angles is essential because they reveal the degree of contact of the phases that exist between liquid water and solid paper surface. Using a glass syringe and filter, 10µL volume drop of deionized water was applied to the surface of uncoated and coated paper substrates of uniform size measuring 1×1 cm in order to quantify CA. Using the Sessile drop technique and a contact angle analyzing instrument (Drop Shape Analyzer 35, KRUSS GndH, Germany), the CA of each sample was determined. Three distinct locations were used for measurements, and average readings were evaluated and presented. The measurement's mean contact angle (CA) fluctuations were under 3°.

2.3.5 Mechanical Properties

2.3.5.1 Tensile testing

The tensile index of coated paper sheets was calculated to investigate the tensile strength (TS) per gram of different coated samples. Horizontal tensile tester machine (Frank PTA GmbHK, Birkanau-Austria) was used for measuring the Tensile index. Samples for the test were made in accordance with the national standards (DIN) ISO 1924-3. The paper ribbons that were 15 cm long and 1.5±0.01 cm in width were clamped in a horizontal manner and put under strain at a rate of 2.5±0.5 cm/min. The readings for different samples were written down and represented in Nm/g. Maximum elongation at break (%) was also obtained from the same instrument while measuring tensile strength. Three samples of each coating recipe were evaluated, and the mean ±standard deviation was reported.

2.3.5.2 Burst strength.

Burst strength is an essential property in evaluating the strength of coated paper, especially for packaging applications during storage and shipping. TAPPI T 807 om-94 standard was used to assess the Burst strength of coated paper sheets. The samples were made with a size of 8×8 cm and then fixed to the Burst tester's annular surface (Messmer Buchel, Netherlands). The rubber diaphragm was then forced to move under hydraulic pressure by a constant flow of liquid moving at 170±15 mL/min. The highest pressure when the clamped samples burst was noted and expressed in kg/cm^2.

2.3.6 Barrier properties

2.3.6.1 Cobb test

The water absorptivity of coated paper sheet was measured using the Cobb test in accordance with the TAPPI 441 om-09 by using a Cobb tester. For testing, samples of 10×10 cm size were prepared and weighed, then placed on the top lid of the Cobb tester over its well. The test for cobb60 and cobb30 was conducted for the 60s and 30s, respectively. To remove the excess water on the surface, the wet paper sample was pressed between two sheets of blotting paper. After getting the final weight, the Cobb60 value was determined using the below-provided equation.

$$\text{Cobb}=(\text{Final weight}-\text{Initial weight})\times 100$$

2.3.6.2 Water vapour transmission rate

The water vapour barrier is one of the most vital aspects in case of food packaging, as the food products cannot sustain high moisture content. To protect the food inside the packaging from moisture, a high moisture barrier is needed. The WVTR of uncoated and coated paper sheets was determined gravimetrically with a vapour permeability cell (6.5 cm in diameter and 2.5 cm depth) (Mercer Instruments, Switzerland) in accordance with ASTM E-96. The paper samples were divided into 8×8 cm squares and fixed to seal the WVTR cell, which containing 18 mL of deionized water. Once WVTR cells were prepared, all of them were arranged in a desiccator set to room temperature of 25° C and 65% RH. At regular intervals of 24 hrs, the weight (Δw) variations of uncoated and coated paper sheets were recorded, and WVTR was determined using the below equation.

$$\text{Water vapour transmission rate}=\Delta w/(\Delta t\times A)(g/cm^2.d\ .day)$$

Where Δw is the weight change, Δt is the required time interval, and A is the sample sheet's area.

2.3.7 Statistical Analysis

IBM SPSS Statistics (Version 28.0.0.0, U.S.A) was utilized to conduct the statistical Analysis on all experimental data presented. A post hoc Tukey test was performed at a 95% confidence interval following a one-way analysis of variance (ANOVA) with a significance level of $p < 0.05$. The measurements were carried out in triplicates and reported as the mean± standard deviation.

3. Results and Discussion:

3.1 Wettability

Hydrophobicity is an important parameter of paper against water penetration, and the contact angle measures the hydrophobicity of the paper surface. The contact angle is the angle between the liquid and the solid surface at the point of contact. A higher contact angle indicates that the surface is less wettable, while a lower contact angle suggests that the surface is more wettable (Kumar et al., 2022). The contact angle images of coated papers with different coating formulations are presented in Fig 3. The uncoated paper showed the lowest contact angle, equivalent to 0° confirming its hydrophilicity. This is due to the penetration of water molecules into the paper through the pores. The high porosity of the paper can be confirmed with the help of FESEM images of uncoated paper.

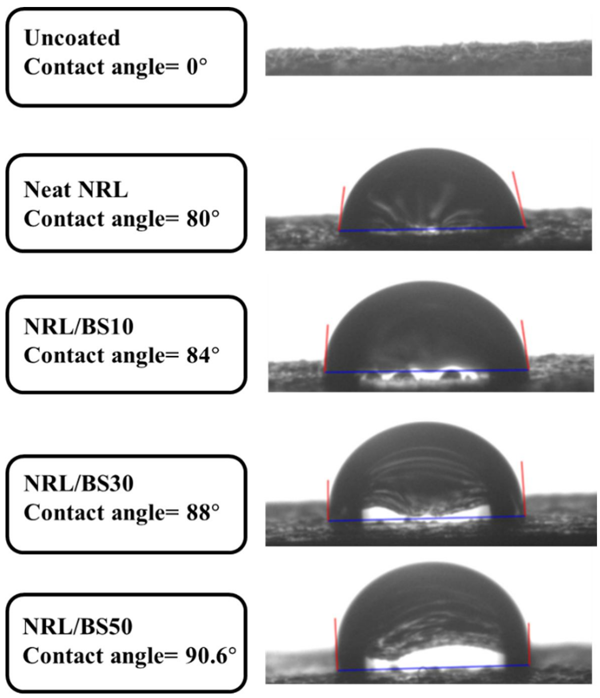


Fig 3. Water contact angle images of paper samples with different coating formulations comprising NRL and butyl stearate

After coating with NRL, the contact angle suddenly raised to 80° showing intermediate wetting behaviour, which is following the results published by Kim et al. in the study of steric acid effects on the properties of natural rubber (Chukwu et al., 2011). This might be due to the filling of paper pores with NRL, which can be inferred from FESEM images. A trend of increasing contact angle with the increase in butyl stearate concentration was observed. This is due to the hydrophobic nature of the butyl stearate molecule. When applied to the surface of the latex, it forms a thin film which reduces the surface energy of the rubber, making it more hydrophobic. This reduced surface energy results in an increase in contact angle (Ann et al., 1985). At 50% butyl stearate concentration, the coated paper's contact angle exceeded 90° showing hydrophobic behaviour. From this result, we can conclude that our coating formulation has the potential to impart hydrophobicity to the paper substrate.

3.2 Barrier Properties

3.2.1 Cobb Test

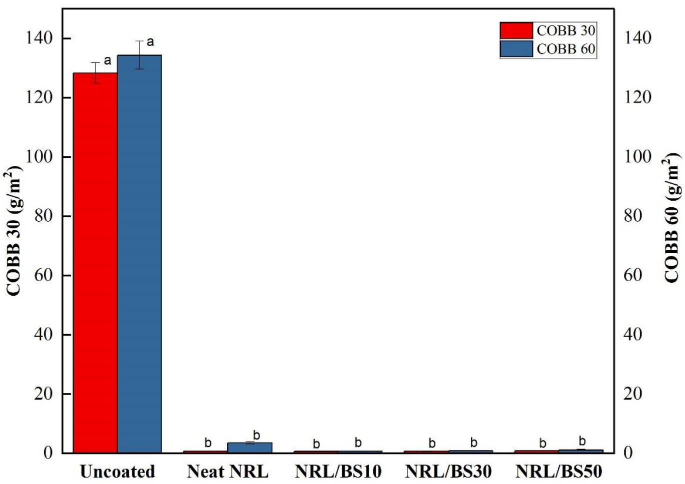


Fig 4. Cobb 30(g/m^2) and Cobb 60(g/m^2) values of uncoated and NRL/BS coated paper samples

The Cobb value is a measure of the absorbency of paper, which is determined by the amount of water that is absorbed by the paper in a specific amount of time(Adams, 1993). The ability of coated papers with different compositions of coating solutions to absorb water after 30 and 60s of exposure was evaluated using the water Cobb value, which has an inverse association with the barrier for water (Letková et al., 2011). Due to the high hydrophilicity, the uncoated paper shows a high-water cobb value (Fig. 4). This high absorbance of water is also due to the high porosity of the uncoated paper, which can be shown from FESEM images. Applying NRL coating has significantly reduced the Cobb value compared to uncoated paper. Both cobb30 and cobb60 values are reduced for almost all coating formulations. Considerable reduction in water absorption is observed due to the hydrophobic nature of NRL and BS and their tendency to repel the water. The filling of paper pores is also a main reason for the drastic reduction in Cobb values of coated paper (Hubbe, 2006). No considerable change is observed in the Cobb values of coated papers with different coating fabrications, and all are nearly in the same range. These results are in accordance with the results produced by, with a sustainable coating of NRL and alpha-1,3 glucan on paper (Adibi et al., 2022a).

3.2.2 Water vapour transmission rate

The moisture barrier plays a crucial role in food packaging applications as food products must frequently deal with moisture(Deshmukh et al., 2023). The degree of resistance to the moisture passage through the coated samples was estimated using the water vapour transmission rate (WVTR) test (Akhila et al., 2023). Two main factors that will affect WVTR are temperature and humidity, which were maintained the same throughout the experimental study of WVTR., the hydrophobic NRL coating layer helped to lower the water vapour adsorption, and it substantially reduced the WVTR of the coated paper sheet (Table 2). This result is consistent with the result published by Adibi et al. for the coating of NRL and MCG on paper (Adibi et al., 2022d). Compared to the controlled sample, all coated samples showed relatively less WVTR values. As expected, with the increase in the amount of butyl stearate, WVTR gradually increased. This increase can be due to the inability of high viscous coating formulation to form a consistent coating layer on the paper surface. Because of this, improperly filled pores may lead to the passage of water vapour and thereby increasing the WVTR.

4. Conclusions

This study showed that NRL, along with the butyl ester of stearic acid, can possibly be utilized in paper coating applications. This butyl stearate was incorporated as a functional additive in the NRL system to create a sustainable hydrophobic coating material. The coated paper characterization indicated that fabricated coatings positively impacted the mechanical properties of paper, such as burst and tensile, which could result from good interactions between the coating layer and cellulosic fibres of the paper substrate. Butyl stearate addition improved the hydrophobicity of the coating formulation. This resulted in a gradual increment in contact angle with the increment in the addition of butyl stearate in the coating formulation. When coated alone, NRL filled the pores properly and showed higher WVTR than the NRL/BS coating, which showed comparatively lower WVTR values. A higher amount of butyl stearate in NRL/BS coating formulations is more favourable to increase hydrophobicity over the mechanical properties, which are somewhat adversely affected. Overall, the NRL/BS coatings showed improved hydrophobicity, barrier for moisture and good mechanical properties, which makes these coatings suitable for food packaging applications. This shows that the investigated NR-BS coating technology may be a desirable choice for eco-friendly paper-based packaging solutions moving towards commercial implementation.

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Table 2. Mechanical and barrier properties of uncoated and NRL-coated paper with different amounts of butyl stearate concentrations.

Sample	Tensile strength (N)	TS index (Nm/g)	Elongation at break (%)	Burst strength (kg/cm^2)	Contact angle (°)	WVTR (g/cm^2.d)
Uncoated	21.04±0.24^{a}	15.41±0.17^{a}	2.68±0.05^{b,c}	9.7±0.18^{a}	0	5.483±0.263^{a}
Neat NRL	38.55±0.99^{c}	28.23±0.73^{c}	3.33±0.01^{c}	10.±0.05^{a}	80.44±0.56^{a}	3.428±0.083^{b}
NRL/BS10	31.16±1.24^{d}	22.83±0.91^{d}	2.58±0.11^{b}	10.±0.13^{a}	84.16±0.36^{b}	3.851±0.282^{b,c}
NRL/BS30	27.66±0.35^{b}	20.26±0.25^{b}	1.92±0.10^{a}	9.3±0.79^{a}	88.20±0.24^{c}	4.225±0.088^{c,d}
NRL/BS50	25.68±0.67^{b}	18.82±0.49^{b}	1.53±0.11^{a}	9.1±0.39^{a}	91.12±0.32^{d}	4.405±0.146^{d}

Values are represented as Mean± Standard deviation obtained from triplicate analysis. Values within the same column having different superscripts a, b, and c significantly differ at $p<0.05$.

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