Effect of tackifier resin and non-rubber components on adhesive property of natural latex

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Abstract. The objective of this study is to better understand the adhesive property of natural latex using phenolic resin at different ratios. Whole natural latex (WNL) and deproteinized natural latex (DPNL) are used. By increasing the resin ratio, the total solid contents (TSC) and viscosity for both types of latex increase. Interestingly, DPNL presents better adhesive properties than WNL for a given resin ratio. The phenolic resin at 3 phr gives the best adhesive property of latex. Beyond this resin ratio, the adhesive property decreases. Nevertheless, the phenolic resin can foster the flow properties in latex during the aging time, thus increasing the adhesive property of latex.

1. Introduction

Natural latex from rubber tree (Hevea brasiliensis) looks like a milky white colloid, it’s dry rubber content or cis-1,4-polyisoprene is about 30-40% floating in the colloid. There are also other components besides rubber present in latex, we call these non-rubber components. So, natural latex consists of 5-6% non-rubber components such as proteins, lipids, carbohydrates, minerals, metal, etc. The effect of such non-rubber constituents on some natural rubber properties have been reported [1-2]. In particular, the non-rubber components can greatly affect the adhesive property of natural rubber. From a practical point of view, this property is of great importance for the natural rubber is frequently used as a matrix in composite materials, for example tires, belts and coated fabrics, or in contact with other solids. It is well-known that natural latex can be used as general glue [3-4], however, the quality of glue from natural latex is not stable due to its non-rubber constituents.

Recently, many chemicals have been added to natural latex to make glue. Most of the formulas are secretive, expensive and have a strong latex smell. When applied to products such as handbags, it can cause allergic reactions in humans. Normally, a fast and convenient way to increase the adhesive property of natural latex is to add the tackifier resin which has many types, such as epoxy resin, vinyl resin, phenolic resin, etc [5-6]. However, epoxy resin and vinyl resin may cause allergic reactions [7-8] but the phenolic resin has no reports of allergic reactions. The phenolic resin is inexpensive and
water-based which is compatible with natural latex. The objective of this study is to find the effect of the phenolic resin and non-rubber components on the adhesive property of natural latex. Two types of natural latex were prepared: whole natural latex (WNL) and deproteinized natural latex (DPNL). The purified natural latex can, more user-friendly, remove the allergen proteins, as more user-friendly.

2. Experimental
WNL and DPNL were prepared from Hevea latex supplied from Thailand, according to a well-defined method [2]. The formulas of adhesive WNL and adhesive DPNL are presented in the table 1 (PR means phenolic resin, KL means 20%wt potassium laurate and KOH means 10%wt potassium hydroxide).

| Formula | C1 | B1 | B2 | B3 | B4 | B5 | C2 | B6 | B7 | B8 | B9 | B10 |
|---------|----|----|----|----|----|----|----|----|----|----|----|-----|
| WNL     | 100| 100| 100| 100| 100| -  | -  | -  | -  | -  | -  | -   |
| DPNL    | -  | -  | -  | -  | -  | 100| 100| 100| 100| 100| 100| 100 |
| PR      | -  | 0.6| 1.8| 3  | 6  | -  | 0.6| 1.8| 3  | 6  | 9   |     |
| KL      | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3   | 3   |
| KOH     | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3   | 3   |

FTIR (Nicolet Magna 850) in Attenuated Total Reflectance (ATR) mode with diamond crystal was used to determine the chemical structure of the rubbers. Nitrogen content of latex samples (WNL and DPNL) was determined using the Kjeldahl method [9]. Total solid content (TSC) of natural latex adhesive were measured following ISO 124. Viscosity of latex was determined by Brookfield Viscometer (LDVD-III, Brookfield, USA) type rational viscometer. The surface energies of the different rubbers and fabrics were evaluated from contact angle measurements using different liquid drops of known properties [2]. Average separation force of two nylon fabrics adhered by adhesive natural latex were recorded on a tensile testing machine (Instron) type peeling test 180º following ASTM 638. Scanning electron microscope or SEM (XL30 Philips, Netherlands) was used to investigate the topology of the fractured surface between the two fabrics adhered by natural latex adhesive. Then, the fractured surfaces were sputter-coated directly with Au/Pd to observe the surface of fabrics. JEOL JSM-5310 at 10kV acceleration voltage.

3. Results and discussion
First of all, WNL and DPNL were cast as a film in order to analyse the presence of non-rubber constituent for both types of latex using FTIR-ATR (spectra are not shown here). It showed clearly that the DPNL has lower intensity of the protein peaks (Amide I at 1660-1630 cm⁻¹ and Amide II at 1575-1480 cm⁻¹) than WNL. This means that WNL contained the protein components, and the contents of these non-rubber constituents were substantially reduced in purification treatment. This result is in good agreement with the previous result [2]. The removal of such non-rubber constituents is important given that some people are allergic to proteins in whole natural rubber. Table 2 shows the measurements of nitrogen content, pH, TSC and viscosity in both WNL and DPNL samples. We found that the quantity of nitrogen content in DPNL is reduced by 82% compared to that of WNL, indicating the protein content can be reduced after the purification of rubber. This establishes confidence in the centrifugation method used here to purify the natural rubber [10]. This result is in good agreement with that of FTIR-ATR. There are no significant differences of the pH, TSC and viscosity between two types of latex.
Concerning to the characterization of adhesive WNL and adhesive DPNL, we found that adhesive WNL samples (formulas C1 to B5) have similar pH values (during 10.3 - 10.4), whatever the quantity of phenolic resin, similar results with those of adhesive DPNL samples (formulas C2 to B10). However, the viscosity value and TSC trend to increase with the increasing of phenolic resin’s concentration, especially beyond 3 phr of phenolic resin in both adhesive WNL and adhesive DPNL.

The surface energy of natural rubbers and fabric can be determined using contact angle measurements. It is well-known that a better knowledge of the adhesion phenomena is required for practical applications of multi-component materials. Moreover, it is considered that adhesion between two solids is due to interatomic and intermolecular forces established at the interface, provided that an intimate contact is achieved [11]. The most common interfacial forces result from van der Waals and Lewis acid–base interactions. The magnitude of these forces can generally be related to fundamental thermodynamic quantities, such as surface free energies of both entities in contact [12]. We found that both types of natural rubber films represent as a non-polar material (below 50 mJ/m$^2$) and nylon fabric represents as a polar material (above 50 mJ/m$^2$), in good agreement with the previous work [13]. Then, the work of adhesion ($W$) between rubber and nylon fabric can be calculated [13]. So, the work of adhesion for the two types of adhesive latex with nylon fabric is fairly similar for all the samples; this may not explain the adhesive property in WNL/nylon ($W = 92.9$ mJ/m$^2$) and DPNL/nylon ($W = 91.2$ mJ/m$^2$) samples.

The adhesive property of adhesive latex (WNL and DPNL) on nylon fabric can be assessed by the average separation force in the same contact area, better adhesive property of adhesive latex does require above average separation force to separate two nylon fabrics. Figure 1 shows the average separation force as a function of adhesive latex formula. The adhesive property of both adhesive latex trends to increase with the increase of phenolic resin concentration until 3 phr (formulas B3 and B8). Beyond this concentration, the separation force decreased. From the topological point of view (SEM images), we can find the insoluble resin beyond 3 phr of resin on the surface of fabric after performing the 180° peeling test, which may cause the decrease in adhesive property of adhesive latex.

| Sample | Nitrogen (%) | pH   | Viscosity (cP) | TSC (%)         |
|--------|--------------|------|----------------|-----------------|
| WNL    | 0.76 ± 0.08  | 10.41| 7.5            | 37.07 ± 0.05    |
| DPNL   | 0.14 ± 0.08  | 11.29| 7.5            | 37.20 ± 0.14    |

Figure 1. Average force for 180° peeling test of nylon fabric coated with samples (formulas C1, B1 to B5 for adhesive WNL and C2, B6 to B10 for adhesive DPNL).
However, adhesive DPNL has higher average separation force than adhesive WNL in the nylon fabric. For a given phenolic concentration and for both types of adhesive latex, the dependence of adhesive property on the nature of latex is observed. The presence of non-rubber components plays a major role in the adhesive property, since the adhesive WNL always presents the weakest adhesive property and the extracted natural latex (adhesive DPNL) always leads to the strongest adhesive property. The reduction of protein components leads, therefore, to an increase of adhesive property. This result indicates a strong dependence of adhesive property on the presence of these components in the natural latex. The possible explanation lies in the presence of proteins within natural latex and, thus, at the interface, affecting the magnitudes of adhesive property. This result is in good agreement with the previous works [2, 10] that migration of low mass components at the surface of natural rubber had occurred. By cleaning with acetone, this surface layer could be removed, resulting in large increase of the adhesion energy of the natural rubber.

4. Conclusions
In this research, we studied the effect of tackifier resin as phenolic resin and non-rubber components in natural latex in order to better understand the adhesive property of adhesive latex. Two types of natural latex were used: whole natural latex (WNL) and deproteinized natural latex (DPNL). We found that nitrogen content in DPNL decreased by 82% compared to that of WNL, while other characteristics were similar to WNL. The increasing of tackifier resin increases the total solid contents and viscosity, thus improves the adhesive property of adhesive latex. Because the tackifier resin could help the flow property in latex during aging time, thus increasing the adhesive property of latex. The adhesive property of adhesive DPNR is better than adhesive WNR due to the removal of non-rubber components which affects the quality of latex. This present research work shows the potential of developing eco-friendly natural adhesive which contains stable quality and less allergen protein.

5. References
[1] Smithhipong W, Chollakup R and Nardin M 2014 (Eds.) In Bio-based composites for high-performance materials, CRC Press, 324 pages.
[2] Smithhipong W, Nardin M, Schultz J, Nipithakul T and Suchiva K 2004 J. Adhesion Sci. Technol. 18 1449.
[3] Chumsamrong P and Monprasit O 2007 Suranaree J. Sci. Technol. 14 269.
[4] Smithhipong W, Nardin M, Schultz J and Suchiva K 2007 Inter. J. Adhesion Adhesives 27 352.
[5] Mess A, Vietzke J-P, Rapp C and Francke W 2011 Anal. Chem. 83 7323.
[6] Sham A and Krishna M 2011 J. Eng. Res. Stu. 62.
[7] http://allergies.about.com/od/contactdermatitis/a/Allergy-To-Bandages-And-Adhesives.htm: July 2018
[8] http://dermnetnz.org/dermatitis/epoxy-allergy.html; July 2018.
[9] Sáez-Plaza P, Michałowski T, José Navas M, García Asuero A and Wybraniec S 2013 J. Crit. Rev. Anal. Chem. 43 178.
[10] Smithhipong W, Tantatherdtam R, Kanokwan R, Suwanruji P, Sriotth K, Radabutra S, Thanawan S, Vallat M-F, Nardin M, Mougin K and Chollakup R 2014 Adv. Mater. Res. 844 345.
[11] Shah DU, Porter D and Vollrath F 2014 Compos. Sci. Technol. 101 173.
[12] Shayestehfar S, Yazdanshenas ME, Khajavi R and Rashidi A-S 2014 J. Eng. Fiber Fabr. 9 158.
[13] Smithhipong W, Suethao S, Shah D and Vollrath F 2016 Polym. Testing 55 17.

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