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Flame Retardant On Ramie Fabric Used Nanobiosilica From Rice Husk Waste

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Abstract:
Indonesia is one of the most important rice producers in the world with 15 million tons of rice husks that have not been optimized for use. Generally, rice husk has a silica content of up to 90-98%. Silica is a halogen-free material that acts as a barrier to prevent heat and mass transfer in the combustion zone. Silica is a compound that has non-toxic and formaldehyde-free flame retardant properties, making it more environmentally friendly. This study aims to develop a flame retardant improvement method using nanobiosilica from rice husk waste and to obtain flame retardant ramie fabric because ramie fiber is a sustainable fiber because of its ecological cultivation process. In this study, ramie fabric was modified using nanobiosilica from rice husk waste with a variation of concentration of 10% and 20% and the amount of 4 and 8 layers to improve fire resistance using the layer-by-layer method. This modification was assisted by a coupling agent 3-aminopropyltriethoxysilane to facilitate the formation of chemical bonds between the nanobiosilica particles and the fabric. The results of the flame retardant test on modified ramie fabric with a concentration of 20% by the amount of 8 layers showed the best fire resistance performance among the others. This ramie fabric can withstand a fire rate of 0 cm/sec for warp direction and 0.04 cm/sec for weft direction. In addition, there is no length of char produced in the warp direction, but in the weft direction it only forms a char about 1 cm long. The washing evaluation result showed that all fabric variations could still retain the flame and the results of the process had a good washing resistance. The SEM analysis showed that the modification of ramie fabric using nanobiosilica was successful even after the washing evaluation was carried out, the nanobiosilica was still attached to the ramie fabric. In addition, the results of the TGA test also show that nanobiosilica can improve the thermal stability of the modified ramie fabric.

Key Word: *Flame retardant, Layer-by-layer, Nanobiosilica, Ramie fabric*

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I. Introduction

Fire-resistant fabric is fabric that can withstand flames so that it cannot continue burning, usually made from asbestos, aramid and nomex fibers. Even though it can naturally withstand flames, using products made from this fiber is less comfortable when worn because it is less breathable. To support the comfort factor, a material is needed that easily absorbs sweat, is cool, not stiff, not rough, and breathable. Comfort is a condition where there is psychological, physiological and physical harmony between humans and the environment[1]. Currently, many researchers have made modifications to cotton fabric to produce good fire resistance because cotton fabric can provide a comfort factor which is one of the most important aspects for apparel products[2]–[10]. However, cotton production in Indonesia still depends on imports because cultivation is difficult. Therefore, to meet the need for industrial raw materials in the long term, there needs to be an alternative solution as a substitute for cotton fiber to meet domestic production so that Indonesia is not dependent on imports. A natural fiber that can be an alternative to cotton fiber is ramie fiber because it has similar properties to cotton fiber, but with the advantage of easier cultivation. Ramie fiber is a sustainable fiber from the ramie plant which has the Latin name *Boehmeria nivea (L.)*. Ramie fiber is the strongest and smoothest fiber compared to other natural fibers in the world. Currently, the ramie plant is being developed in Indonesia by the Indonesian Ramie Consortium (KORI) following up the appointment of ramie plant as a National Research Priority (PRN) in 2020-2024[11]. To be able to have good fire resistance functionality in ramie fabric, the ramie fabric needs to be chemically modified with a flame retardant substance.

Indonesia is one of the main rice producers in the world, producing around 75 million tons of dry milled grain per year or the equivalent of 15 million tons of rice husks which has not been used optimally[12], even though rice straw contains more silica than other plants. Generally, the silica percentage in rice husks reaches 90-98% of its composition[13]-[14]. Rice husks are non-flammable and difficult to ignite with fire while being in an open space unless air is blown into them[15]. Silica is a material that is halogen-free and acts as a barrier, preventing heat and mass transfer in the combustion zone[16]. Besides that, silica can form a protective layer and provide thermal stability to the material[17]. The silica found in rice husks is a compound that has fire-resistant properties that are non-toxic and formaldehyde-free. The natural silica found in agricultural waste can be used as an alternative to commercial silica base materials[12], because it is considered more environmentally friendly. Silica from agricultural waste is renewable, economical, abundant, and its use is still less than optimal in Indonesia[14], especially in the textile industry. One of the uses of nanobiosilica in the textile industry is that it can be used as a material to increase the flame retardant properties of fabric that has been treated. Nanobiosilica from rice husks is a renewable and sustainable material because it is considered biomass waste that can be reused. Therefore, the purpose of this research is to study the use of nanobiosilica from rice husk waste as an environmentally friendly alternative flame retardant material for improving the flame retardancy of cellulose-based fabrics. This research aims to develop a method for improving fire resistance by using nanobiosilica from rice husk waste and obtaining fire-resistant ramie fabric.

Silica is strongly reputed to work on the surface of the material in its action to provide fire resistance properties to the material. In accordance with the premise above, it is possible that an effective application method for improving fire resistance on textile materials is by layer-by-layer. If done using the pad-dry-cure method as is usually done in industry, there is a possibility that this method will not be effective for nano-sized silica particles because the nanobiosilica particles will easily enter the fiber structure. In fact, its work is expected to be outside the fiber as a thermal barrier when in contact with fire. The process carried out in this method is considered environmentally friendly because it does not require a lot of solution to be used. Apart from that, preparation in the textile sector is still easy, simple and energy-efficient[19]. There are several LBL process techniques that can be carried out on fabric, one of which is the immersive assembly technique as used in this research. This technique is done by soaking a fabric in a solution that has a positive or negative charge. After that, the fabric is rinsed and dried, then soaked again in a solution that has a different charge from the previous solution, then rinsed and dried again. This process is repeated until the desired number of layers is achieved. There are several factors that can influence the results of this method, among them are: electrolyte concentration, ionic strength, temperature, absorption time, rinsing and drying time[19], pH, heat, solvent, mechanical forces, competitive binding, and salts[20].

In previous research, several researchers still used silica precursors such as TMOS, TEOS, and tetrabutylorthosilicate as well as other commercial materials for applying flame retardant enhancements to fabrics. Whereas, those precursors mentioned above is hazardous for human health. Research conducted by Kashiwagi et al (2000) reported that silica fume and silica gel can accumulate on the surface of the polymer to act as a thermal insulation layer and reduce the polymer concentration near the surface[21]. He also confirmed the existence of relationship between the viscosity of the polymer and the surface area of the silica particles which has a significant impact on the combustion properties. Attia et al (2015) applied silica nanoparticles from rice husk waste and organic borates using a binder on linen fabric with a back coating technique which resulted in a high level increase in flame retardant textile fabrics[22]. Przybylak et al (2016) applied organosilicon derivatives to cotton fabrics to efficiently provide a high flame retardant protective layer by producing high reactivity and cross-linking for the function of siloxane groups in increasing washing resistance and thermal stability[23]. Saleemi et al (2020) modified polyester/cotton fabric using SiO2 and ZnO nanoparticles which resulted in increased fire resistance with the addition of silica nanoparticles[10]. Malucelli (2020), with the applying of silica nanoparticles to cotton fabric using the layer-by-layer method, showed excellent results in reducing burning time[9]. Now, in this research, a coupling compound of the aminopropyltriethoxysilane type was used to facilitate the formation of chemical bonds between nanobiosilica particles and fabric by varying the concentration of nanobiosilica and the number of layers to be applied to the ramie fabric. Therefore, it is hoped that the greater the number of layers and the higher the concentration of NBS applied can produce better fire resistance properties using the LBL method.

II. Material And Methods

Material: Ramie fabric with 100% ramie fiber composition, plain woven type with a grammage of 411.1 g/m^2. Nanobiosilica from rice husks was obtained from the Bogor Post-Harvest Research and Development Center and PT Agro Industri, Dispertion (PT Tanatex), 3-Aminopropyl triethoxysilane (Sigma Aldrich), acetic acid (Merck), sodium hydroxide (Merck), distilled water (PT Amidis Tirta Mulia), ethanol (CV Seger Chemical).

Tools: Goblets, measuring cups, Erlenmeyer, measuring pipettes, stirring rods, analytical balances, universal pH indicators, magnetic stirrers, hot plate stirrers (WiseStir), and ultrasonic cleaners (Power Sonic 420) in the Environmental Testing Laboratory of the Textile Center. Sonicator (Janke & Kunkel), compressor, padder and stenter at the STTT Bandung Polytechnic Improvement Laboratory.

Study location: This research methodology was carried out at the Environmental Testing Laboratory at the Textile Center; Refinement Laboratory, FTIR Characterization Laboratory, Chemical Evaluation Laboratory, Physics Evaluation Laboratory at Polytechnic of Textile Technology; SEM Instrument Laboratory at the Geological and

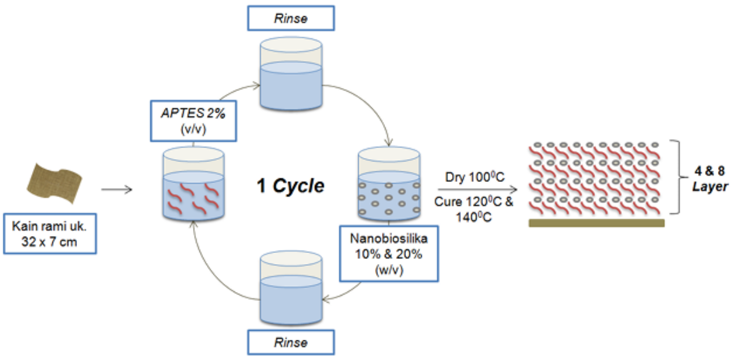
Marine Research Center; as well as the Chemical Instruments Laboratory of the Indonesian Education University, Bandung.

Procedure methodology

The first thing that needs to be prepared is to make a nanobiosilica solution from rice husk waste which is done in three stages in the way that previous researchers have done[24] with some modifications. The working procedure for making NBS solution is as follows: (1) Make pH water in an alkaline atmosphere as an NBS solvent by adding 100 ml of NaOH to distilled water until the pH reaches 11; (2) Add 2% (v/v) dispersant to pH 11 water while stirring gently using a stir stick; (3) Then add NBS with concentrations of 10% and 20% (w/v) to the solvent while stirring on a hot plate stirrer (WiseStir) at a speed of 1200 rpm, at a temperature of 80^0C for 30 minutes; (4) After that, the NBS solution was ultrasonicated at 70^0C for 2 hours with a frequency of 40 KHz.

The next preparation is to make a coupling agent solution using APTES which is carried out in two stages using the method that researchers have carried out previously[25] with some modifications. The working procedure for making the APTES solution is as follows: (1) Make a mixture of ethanol and water (60:40 ml) with the addition of acetic acid (CH3COOH) so that the solution is at pH scale of 4.5 - 5.5. (2) After that, add APTES as much as 2% (v/v) drop by drop while stirring at a speed of 350 rpm for 10 minutes.

After making the solution, the solution is immediately applied to the fabric using the LBL method which is expected to produce cross-linking in layers between the fabric and NBS assisted by the APTES coupling agent. The working procedure for applying NBS and APTES solutions to ramie fabric using the LBL method (can be seen in Picture no1) is as follows: (1) Prepare samples of ramie fabric that have been cut to proper size for flame retardant vertical method testing; (2) The ramie fabric is soaked in the APTES solution for 5 minutes; (3) After that, rinse the ramie fabric with deionized water for 2 minutes; (4) Then the fabric is dried in a stenter machine at a temperature of 100^0C for ±10 minutes; (5) After the fabric is dry, continue heating it at 120^0C for 3 minutes; (6) Continue by placing the heat-cured ramie fabric in the NBS solution with a concentration of 10 & 20% (w/v) for 5 minutes; (7) The ramie fabric was rinsed with deionized water for 2 minutes; (8) Then the fabric is dried in a stenter machine at a temperature of 100^0C for ±20 minutes; (9) After the fabric is dry, continue heating the preservation at 140^0C for 3 minutes; (10) Repeat all these stages according to the layers you want to achieve (4 & 8 layers), but continue with soaking in APTES and NBS solutions for 2 minutes and each rinse for 30 seconds.



Picture no1: Illustration of Layer by Layer Methods on Ramie Fabric-APTES-Nanobiosilica

Surface Chemical Analysis with FTIR

Fourrier Transform InfraRed (FTIR) is an instrument used to analyze the presence of functional groups in the samples being tested. Analysis is carried out by looking at the shape of the spectrum or specific peaks which indicate the type of functional group the compound has[26]. Characterization using FTIR was carried out to analyze the fabric qualitatively by proving the presence of functional groups in ramie fabric that had been treated using NBS and APTES. The material used in this characterization test is ramie fabric consisting of (a) untreated fabric (blanko fabric), (b) fabric that has been modified with NBS and APTES, and (c) modified fabric that has been washed.

Surface Morphology Analysis with SEM

Scanning Electron Microscopy (SEM) is an instrument with an effective method for analyzing organic and inorganic materials on the nanometer (nm) or micrometer (μm) scale[27]. From the results of analysis using SEM, the size and shape of the particles of a material can be determined if the sample is in powder form and also identify the fiber morphology from the success of a coating in the form of coated fabric. The material used in this characterization test is ramie fabric measuring 0.5 x 0.5 cm consisting of (a) untreated fabric (blanko fabric), (b) fabric that has been modified with NBS and APTES layers, and (c) modified fabric that has been washed.

Flame Retardant Vertical Method Testing

The flame retardant vertical method testing is one of the tests carried out to test textile materials whether they are able to withstand flame or whether they are flammable. The principle of testing fire resistance using the vertical method is to burn fabric that is clamped to a frame and placed vertically for a certain time. The time from when the fire is taken until the flame goes out, the time from when the flame goes out until the coals are extinguished and the length of the char in the sample are measured. The materials used in this test were test samples by measurement of 32x7 cm, both warp and weft.

Washing Evaluation with Repeated Washing

In this washing evaluation, the aim is to determine the resistance of the treated fabric to repeated washing, whether it still has the same performance as the treatment results or whether its performance decreases after washing. The principle of washing evaluation is that the test sample is washed in a washing solution with 4 g/l AATCC soap under certain conditions, then rinsed and dried. In this evaluation, the washing temperature were 40^0C for 45 minutes without any pH adjustment. The material used in this test is a test sample by measurement of 2.5x20 cm.

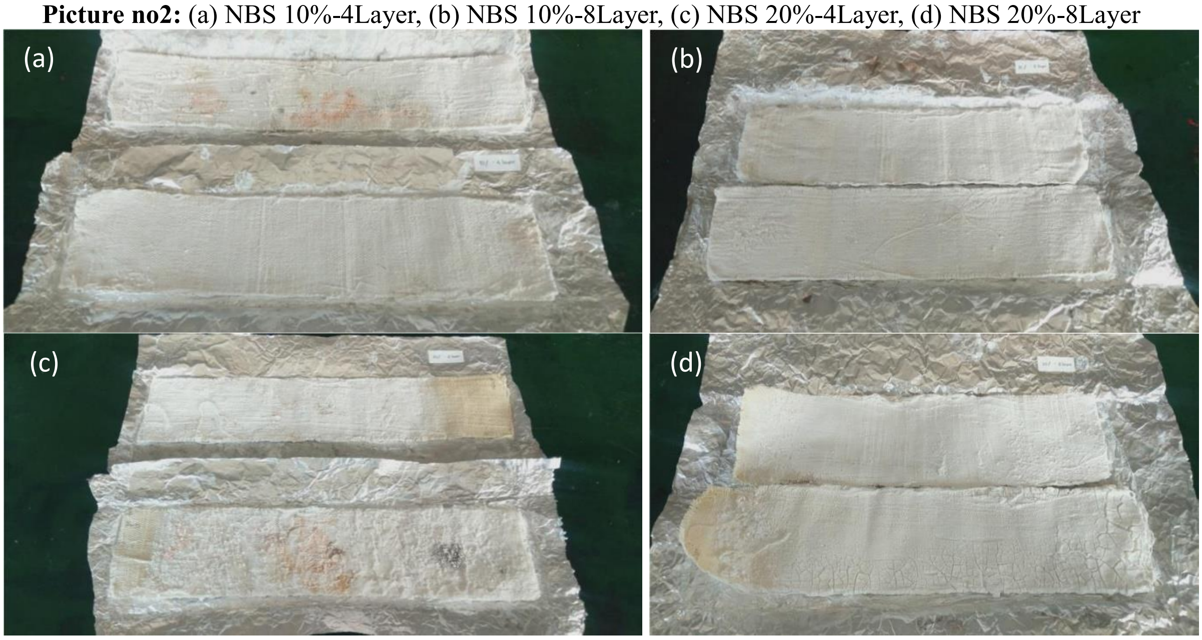
Thermo Gravimetry Analysis (TGA) Testing

Thermo Gravimetry Analysis (TGA) is an instrument used to analyze mass changes in a sample which is measured as a function of temperature. This test can not only analyze the thermal and residual stability of fabrics that have been modified using flame retardant compounds which begin to be measured when heated at room temperature to high temperatures at 600^0C in nitrogen (N_2) and atmospheric (O_2) conditions, but can also analyze up to temperatures 1000^0C. The initial temperature used for this test was set at 25^0C and ended at 850^0C with a rate of 10^0C/min under nitrogen conditions. The material used in this test is ramie fabric consisting of (a) untreated fabric (blanko fabric), (b) fabric that has been modified with NBS and APTES coating, and (c) modified fabric that has been washed. The weight of each blanko ramie fabric sample used in this test was 43.685 mg, the modified ramie fabric was 56.341 mg, and the washed ramie fabric was 58.826 mg.

III. Result

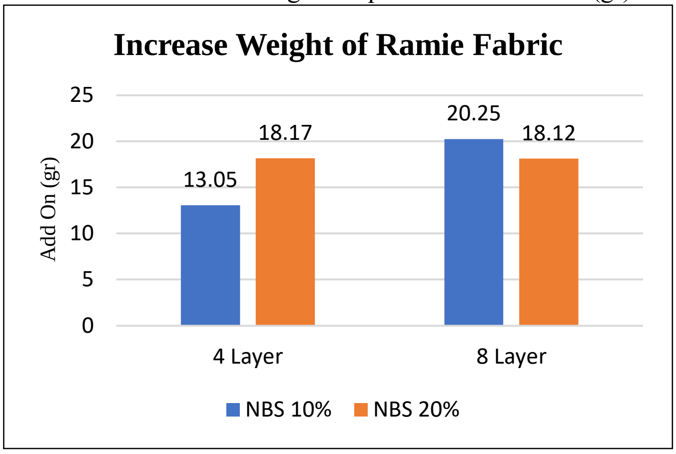
Results of Layer by Layer Method: From the results of applying the NBS solution to Picture no2 with a concentration of 10% on ramie fabric with a total of 4 layers, it can be seen that the coating is visually more even compared to application at a concentration of 20%. At meanwhile, from the results of applying NBS solutions with concentrations of 10% and 20% on ramie fabric with a total of 8 layers, it can be seen that the results of both coatings are quite even visually, the same as the results of coating 4 layers with a concentration of 10%.

Picture no2: (a) NBS 10%-4Layer, (b) NBS 10%-8Layer, (c) NBS 20%-4Layer, (d) NBS 20%-8Layer



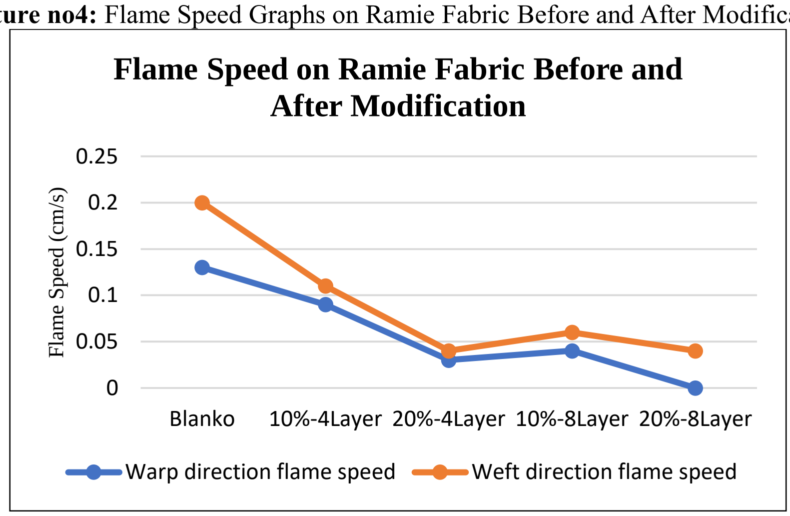
Picture no3 shows the results of weighing ramie fabric before and after modification using NBS using the Layer by Layer method. Here, it can be seen that the post-modified fabric does not always show an increase in fabric weight even though the number of layers applied is increased. This can happen because when ramie fabric is rinsed after being soaked in the NBS solution, some of the NBS that has previously adhered to the fabric is released.

Picture no3: Increase Weight Graphs of Ramie Fabric (gr)



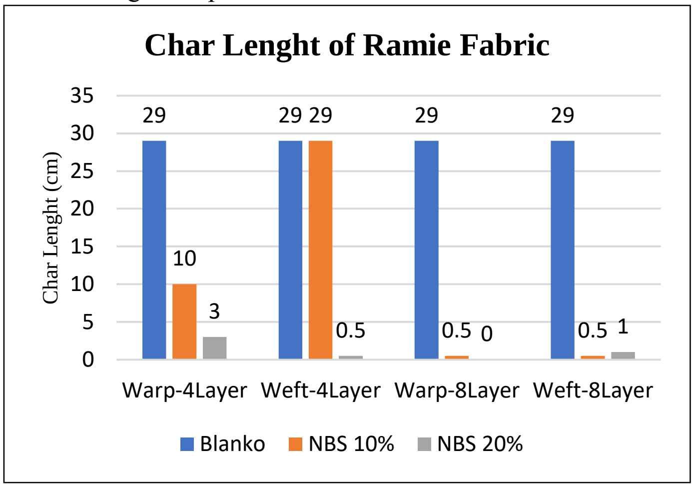
Results of Flame Retardant Vertical Method Test: Picture no4 shows a graph of the flame rate on ramie fabric both before and after modification. It can be seen that the flame rate graph decreases as the concentration and number of NBS layers applied to the ramie fabric increases. In a sample of ramie fabric modified using NBS with a concentration of 20% by quantity of 8 layers, the fire was immediately extinguished as soon as the fire source was removed from the fabric.

Picture no4: Flame Speed Graphs on Ramie Fabric Before and After Modification

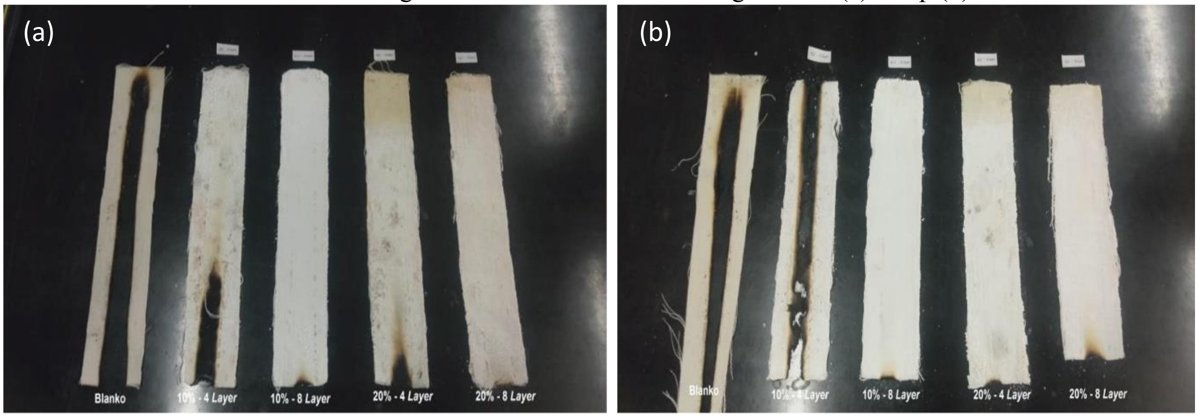


Picture no 5 shows a graph of the length of char produced from burning ramie fabric both before and after modification. In Picture no6, it can be seen that the blanko ramie fabric, both in the warp and weft directions, has a length of char along the ramie fabric sample because it was not modified so the ramie fabric burned completely. At meanwhile, in ramie fabric that has been modified using NBS, it can be seen that the length of char produced is little or even non-existent.

Picture no5: Char Length Graphs of Ramie Fabric Before and After Modification



Picture no6: Char Length of Ramie Fabric After Being Flamed (a) Warp (b) Weft

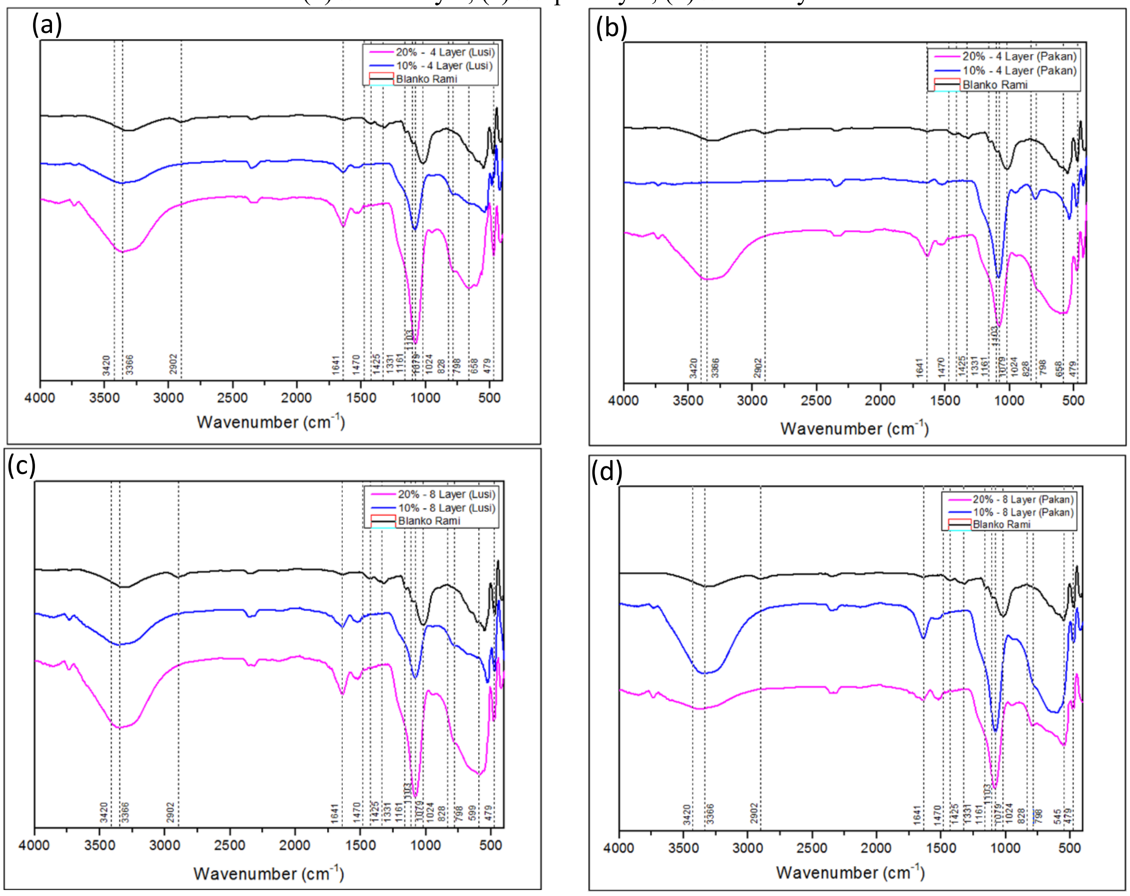


Results of Washing Evaluation: Based on the washing results of the ramie fabric in Picture no7, it can be seen that the fabric became damaged after the washing process was repeated five times. Ramie fabric that has undergone the washing process is burned manually without using a flame retardant vertical method testing equipment due to limited test samples. It can be seen that after this washing evaluation the modified fabric can still withstand the rate of fire because the ramie fabric does not burn completely. In addition, it can be seen that the ramie fabric only forms short char length.

Results of Fourier Transform Infrared Spectroscopy (FTIR) Characterization: Picture no8 shows the results of characterization of ramie fabric modified with nanobiosilica using APTES compared to blanko ramie fabric using FTIR. It can be seen that in the modified ramie fabric there is a strong absorption band in the area around 1095 – 474 cm^{-1} which indicates the presence of several functional groups Si-O-Si in nanobiosilica. The absorption band 1103 cm^{-1} can be caused by the asymmetric mode of siloxane, 798 cm^{-1} is caused by the symmetric mode of silanol, and 479 cm^{-1} is caused by bending of SiO_2. The absorption band in the 3400 cm^{-1} area shows the presence of amine groups (NH_2) in nanobiosilica treated with APTES. The absorption bands in the 3300 cm^{-1} and 1600 cm^{-1} areas can be caused by the presence of OH groups from silanol and bending vibrations from the absorbed water molecules. The absorption band in the 1470 cm^{-1} region shows CH bending of the propyl amino silane groups attached to the APTES-treated nanobiosilica.

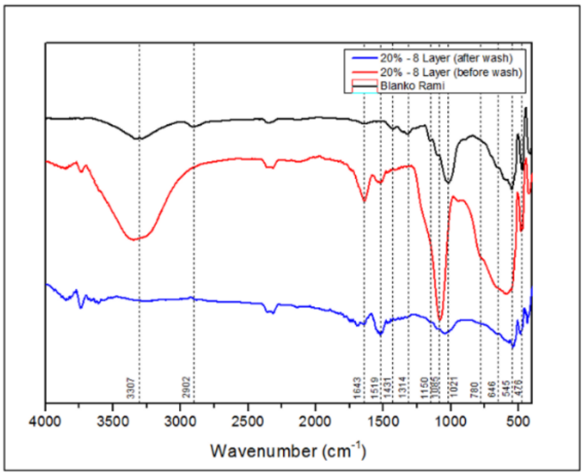
Picture no7: Results of Washing Evaluation on Ramie Fabric After Modification

Picture no8: Results of FTIR Characterization on Ramie Fabric Before and After Modification (a)Warp-4Layer, (b)Weft-4Layer, (c)Warp-8Layer, (d)Weft-8Layer



Picture no9 shows the results of FTIR characterization of ramie fabric which has optimum fire resistance test results, which is at 20% NBS concentration for 8 layers both before and after washing compared to blanko ramie fabric. Here, it can be seen that the ramie fabric that has passed through washing evaluation has a low absorption intensity. This shows that the concentration of NBS applied to the fabric decreases after continuous friction occurs during the washing process. However, here is still an absorption band in the area 1095 – 474 cm^{-1} which shows that there are still several Si-O-Si functional groups in the NBS.

Picture no9: Results of FTIR Characterization on Ramie Fabric Before and After Washed

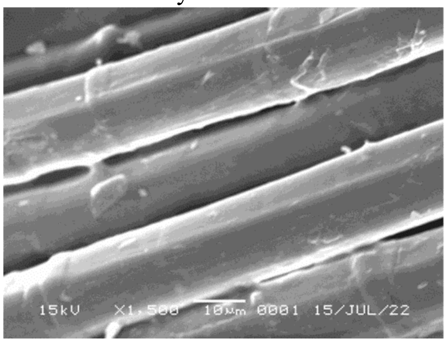


Results of Scanning Electron Microscopy (SEM) Analysis: This analysis was carried out only on ramie fabric that had optimum fire resistance test results, namely NBS with a concentration of 20% in 8 layers. Picture no10 shows the surface morphology of unmodified ramie fiber which has a smooth surface but a slightly rough texture.

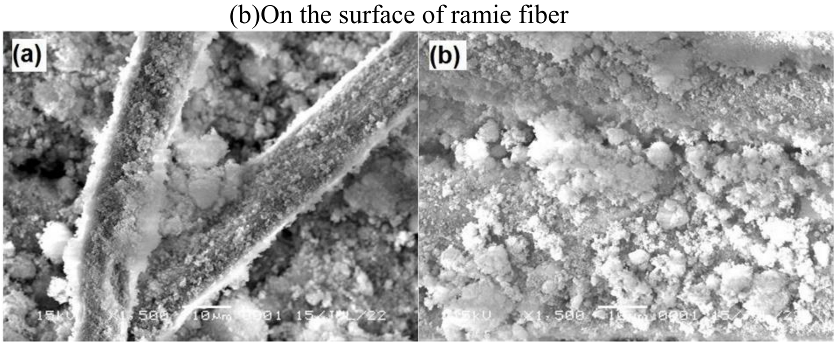
Picture no11 shows the results of analysis of modified ramie fabric, it can be seen that the surface morphology of the ramie fiber is covered with NBS particles that have coated the fabric. Here, the change in surface morphology is very visible when compared to ramie fabric that has not been modified. The results of this analysis show that the NBS particles applied to ramie fabric are not homogeneous.

Picture no12 shows the results of the analysis of ramie fabric which has been washed and evaluated. It can be seen that the surface morphology of the ramie fiber is still covered with NBS particles coating it but it is thinner than the surface of the modified ramie fabric. This condition shows that the NBS still adheres well to the ramie fabric even though washing evaluation has been carried out. This is proven by the results of fire resistance tests on washed ramie fabric.

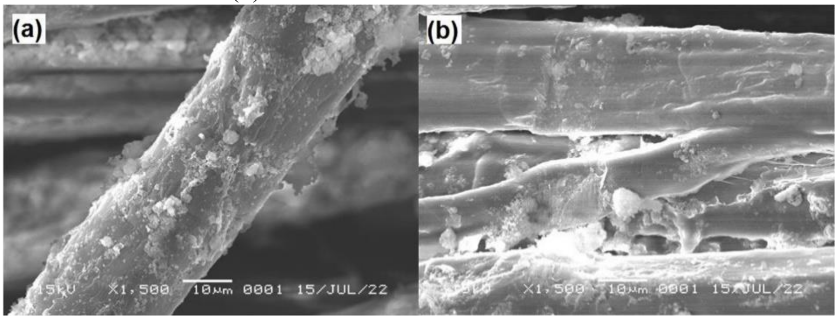
Picture no10: Results of SEM Analysis on Ramie Fabric Before Modification



Picture no11: Results of SEM Analysis on Ramie Fabric After Modification (a)Inside the surface of ramie fiber (b)On the surface of ramie fiber



Picture no12: Results of SEM Analysis on Ramie Fabric After Washed (a)Inside the surface of ramie fiber (b)On the surface of ramie fiber



Results ofThermo Gravimetry Analysis (TGA) Test: This test is carried out only on ramie fabric that has optimum fire resistance test results, namely NBS with a concentration of 20% in 8 layers. The initial temperature used for this test was set at 25^0C and ended at 850^0C with a rate of 10^0C/min under nitrogen conditions. Picture no13 and Table no1 show that there was a weight loss of 67.4% that occurred in blanko ramie fabric starting at temperatures between 717.52 to 761.37^0C. This weight loss can occur due to decomposition of cellulose with a maximum decomposition rate at a temperature of 715.83^0C. Apart from that, the main cause of weight loss in ramie fabric is due to the evaporation of water and volatiles.

In the TGA test results for modified ramie fabric, it can be seen that one stage of decomposition started to occur at a temperature of 551.55 to 559.71^0C with a weight loss percentage of 56.55%. This weight loss can occur due to decomposition of hemicellulose with a maximum decomposition rate at a temperature of 572.91^0C. The energy produced from TGA testing on modified ramie fabric is an exothermic reaction with a value of -23.4 J.

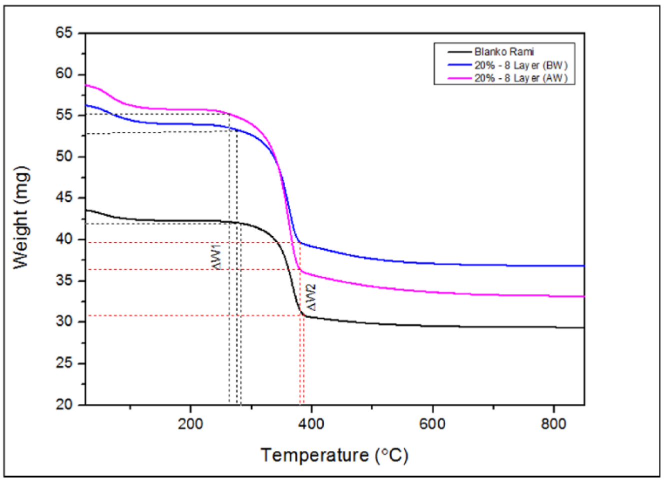
In the TGA test results for washed ramie fabric, it can be seen that one stage of decomposition started to occur at a temperature of 522.76 to 534.17^0C with a weight loss percentage of 65.49%. This weight loss can occur due to decomposition of hemicellulose with a maximum decomposition rate at a temperature of 558.06^0C. The energy produced from the TGA test on washed ramie fabric is in the form of an exothermic reaction with a value of -25.26 J.

Table no1: Onset, Offset, Peak, and Weight Loss Data

	Blangko	20% -8 Layer (BW)	20% -8 Layer (AW)
Peak (^{0}C)	715,83	572,91	558,06
Onset (^{0}C)	717,52	551,55	522,76
Offset (^{0}C)	761,37	559,71	534,17
Heat (J)	32,45	-23,4	-25,26
Weight (%)	67,4	56,55	65,49

***Notes:** Tonset = First decomposition temperature (hemicellulose decomposition)
Tpeak = Maximum decomposition rate
Toffset = First decomposition from last process (ligini decomposition)

Picture no13: TGA Test Curves on Ramie Fabric Before and After Washed



IV. Discussion

When NBS solutions with different concentrations and number of layers were applied to ramie fabric, it was seen that the resulting layers were visually uneven. This can happen because the NBS solution with a concentration of 20% has a high viscosity to the point that is very thick like a paste, making it difficult to soak and spread the NBS onto the fabric in the solution.

According to four variations applied to ramie fabric, all of the modified fabrics have varying unevenness in the coating. This becomes less accurate if it is caused by the large number of layers applied to the fabric. There are several factors that influence the unevenness of the coating on the modified ramie fabric, one of which is that the viscosity of the solution is too thick, resulting in the coating on the fabric becoming uneven and looking cracked like very dry soil. The resulting layer that looks cracked can be caused by high drying temperatures and long drying times. Therefore, a proper drying process must be carried out on NBS-modified ramie fabrics. Silica dries very easily because silica has large porosity, which means it can absorb water and humidity around it. By these facts, silica products are usually used as a dryer. If the drying process on NBS-modified ramie fabric is too long, the NBS solution applied to the fabric can become powder granules again.

The weight of ramie fabric during weighing also increases or decreases for each layer. Researchers assume that this can happen because APTES evaporates with ethanol during the drying process, so that the adhesion between NBS and APTES is reduced. Increasing the number of layers applied to the fabric can affect the test results for air permeability and stiffness of the fabric.

In a sample of ramie fabric modified using NBS with a concentration of 20% with 8 layers, the fire was immediately extinguished as soon as the fire source was removed from the fabric. This means that ramie fabric with a 20% NBS concentration of 8 layers has excellent fire resistance performance because it is able to withstand flames and not continue the burning. This condition shows that the higher the concentration of NBS used and the greater the number of layers on the modified fabric, the better its fire resistance performance. This can happen because the high concentration of NBS used can increase the thermal insulation properties and the large number of layers of NBS that coat the ramie fabric means that the barrier properties to protect the substrate underneath are better because the distance from the surface being coated is farther. Therefore, the higher the concentration and the greater the number of layers applied using the layer by layer method, the better the performance obtained.

Researchers assume that the reaction occurring between the NBS and the ramie fabric (ramie fabric can withstand flames) is a physical reaction because the NBS coats the outer surface of the ramie fabric which functions as a thermal protective barrier. If a chemical reaction really occurs between the ramie-APTES-NBS fabric, then it will still produce good fire resistance performance even after the washing evaluation process is carried out on the modified ramie fabric.

In the fire resistance test, the entire fabric of unmodified ramie burned completely, but in ramie fabric that has been modified using NBS, little or no char was produced. This proves that NBS can prevent heat transfer in areas affected by combustion as previously reported[16]. In addition, NBS can inhibit volatiles from evaporating into the atmosphere so that they do not continue burning as previously reported[28].

Based on the results of the washing evaluation, the appearance of the ramie fabric was damaged due to repeated washing for five times. This is because ramie fabric has fine and slippery fibers so it easily breaks down when exposed to continuous friction. It is best to sew the edges of the ramie fabric before washing the ramie fabric so that it does not unravel. After trying to burn it manually, the modified ramie fabric that had been washed was still able to withstand the flame and even only formed a short length of char. This can be interpreted that the NBS applied to the ramie fabric is still bonded well because of the help of APTES as a coupling agent. Researchers assume that the curing process for APTES is very important so that APTES can bond the ramie fabric and NBS properly because it can affect the washing evaluation process. In this research, a good chemical reaction occurred between ramie-APTES-NBS fabric because ramie fabric that had been washed still produced good fire resistance performance.

Based on the FTIR characterization results, it can be seen that the higher the NBS concentration used, the stronger the absorption intensity. In fact, the absorption intensity is also influenced by the number of layers applied to the ramie fabric. However, ramie fabric modified with 10% NBS concentration in 4 layers, did not have absorption bands in the 3300 cm^{-1} and 1600 cm^{-1} areas. This shows that there are no OH groups from silanol and bending vibrations from water molecules absorbed by NBS. This condition is in accordance with the results of the fire resistance test, where the weft ramie fabric modified with a 10% NBS concentration of 4 layers burned completely. On the other hand, ramie fabric in the weft direction of 8 layers with the same concentration, where the fabric has an absorption intensity in the 3300 cm^{-1} and 1600 cm^{-1} areas, the fabric is stronger than ramie fabric modified with an NBS concentration of 20%. This is also in accordance with the fire resistance test conditions, where weft ramie fabric modified with 10% NBS concentration in 8 layers has a shorter char length compared to 20% NBS concentration. After washing evaluation, the wave absorption intensity becomes low. This shows that the concentration of NBS applied to the fabric decreases after continuous friction occurs during the washing process.

Based on the results of SEM image analysis, the difference between the fiber surface morphology before and after modification is clearly visible. The morphology of the modified fiber shows that the entire surface is coated with inhomogeneous NBS particles. This can be caused by the viscosity of the solution being too thick and also the coating on the fabric being uneven, resulting in lumps and flakes on the surface of the ramie fabric fibers. After washing evaluation, it was seen that the surface morphology of the fiber was still coated with NBS particles even though they were thinner. This shows that the coupling agent used has succeeded in bonding the ramie fabric and NBS very well as proven by the results of the fire resistance test after repeated washing.

Based on the TGA test results, it can be seen that at a temperature of 522.76^0C, ramie fabric has experienced decomposition. The initial temperature of decomposition (T_{onset}) in ramie fabric that has been evaluated for washing decreased earlier compared to modified ramie fabric. This shows that NBS applied to ramie fabric can influence the decomposition temperature. This means that the greater the amount of NBS applied to the fabric, the initial decomposition temperature (T_{onset}) will increase. Likewise, looking at the maximum decomposition rate (T_{peak}), the temperature of ramie fabric after washing process is 558.06^0C while the temperature of ramie fabric before washing process reaches 572.91^0C. The greater the amount of NBS applied to the fabric, the maximum decomposition rate (T_{peak}) will also increase. However, in Table no1 it can be seen that the initial decomposition temperature (T_{onset}) of blanko ramie fabric is 717.52^0C. This temperature appears to be greater than the initial decomposition temperature (T_{onset}) of washed ramie fabric or even modified ramie fabric.

In this TGA curve, weight loss in blanko ramie fabric occurs when it is less than 45 mg with a weight loss percentage of 67.4%, while modified ramie fabric and washed ramie fabric have a weight loss percentage of 56.55% and 65.49% respectively. The weight loss percentage value shows that blanko ramie fabric experienced more weight loss compared to modified ramie fabric and washed ramie fabric. This is because the blanko ramie fabric is not applied by NBS which is able to work as a barrier layer to protect the ramie fabric from exposure to fire. In the energy column (J), the blanko ramie fabric experienced endothermic reaction (heat absorption), while the modified ramie fabric and the washed ramie fabric experienced exothermic reaction (heat release). By the test result, it is assumed that the ramie fabric crystallizes due to the application of NBS. Therefore, it can be concluded that NBS can improve the thermal stability of ramie fabric by releasing heat due to its properties as a protective barrier and thermal insulation. This shows that colloidal silica is able to reduce burning and has been successfully applied using the LBL method, where the aggregation of particles on the surface of the fabric can form an insulating layer which will limit heat transfer[2].

V. Conclusion

It can be reported that nanobiosilica from rice husk waste is able to provide good fire resistance to cellulose fiber, especially ramie fiber with optimum coating. The optimum coating itself can be reached in varying concentrations of 20% nanobiosilica solution in 8 layers which can withstand the rate of fire very well, proven by the fire rate of 0 cm/s for the warp direction and 0.04 cm/s for the weft direction and the char length is only 1 cm or even no char at all.

An effective way to apply nanobiosilica to ramie fabric to produce optimal fire resistance is by using the layer-by-layer method, a high concentration of nanobiosilica, the process of making a nanobiosilica solution using ultrasonication, as well as several process parameters such as setting the temperature for stirring the nanobiosilica solution, ultrasonication process time, drying temperature, and heating temperature of the coupling agent.

Factors that can influence the results of flame retardant enhancement using nanobiosilica on ramie fabric in this research are the concentration of the solution and the number of layers applied to the fabric. These two factors can provide good fire resistance performance in ramie fabric.

References

[1] A. Das and R. Alagirusamy, *Science in fabricing comfort*. Woodhead Publishing Limited, 2010. doi: 10.1533/9780857092830.

[2] G. Laufer, F. Carosio, R. Martinez, G. Camino, and J. C. Grunlan, "Growth and fire resistance of colloidal silica-polyelectrolyte thin film assemblies," *J Colloid Interface Sci*, vol. 356, no. 1, pp. 69–77, Apr. 2011, doi: 10.1016/j.jcis.2010.12.072.

[3] Z. Yang, X. Wang, D. Lei, B. Fei, and J. H. Xin, "A durable flame retardant for cellulosic fabrics," *Polym Degrad Stab*, vol. 97, no. 11, pp. 2467–2472, 2012, doi: 10.1016/j.polymdegradstab.2012.05.023.

[4] K. Xie, A. Gao, and Y. Zhang, "Flame retardant finishing of cotton fabric based on synergistic compounds containing boron and nitrogen," *Carbohydr Polym*, vol. 98, no. 1, pp. 706–710, 2013, doi: 10.1016/j.carbpol.2013.06.014.

[5] A. El-Shafei, M. Elshemy, and A. Abou-Okeil, "Eco-friendly finishing agent for cotton fabrics to improve flame retardant and antibacterial properties," *Carbohydr Polym*, vol. 118, pp. 83–90, Mar. 2015, doi: 10.1016/j.carbpol.2014.11.007.

[6] C. K. Poon and C. W. Kan, "Effects of TiO2 and curing temperatures on flame retardant finishing of cotton," *Carbohydr Polym*, vol. 121, pp. 457–467, May 2015, doi: 10.1016/j.carbpol.2014.11.064.

[7] C. Kasipah, R. Yulina, W. Septiani, Rr. S. Gustiani, and M. D. Sukardan, "APLIKASI KITOSAN-FOSFAT UNTUK MENINGKATKAN SIFAT TAHAN API KAIN KAPAS," *Arena Tekstil*, vol. 34, no. 2, 2019, doi: 10.31266/at.v34i2.5196.

[8] D. Xu *et al.*, "Preparation and mechanism of flame-retardant cotton fabric with phosphoramidate siloxane polymer through multistep coating," *Polymers (Basel)*, vol. 12, no. 7, Jul. 2020, doi: 10.3390/polym12071538.

[9] G. Malucelli, "Sol-Gel and layer-by-layer coatings for flame-retardant cotton fabrics: Recent advances," *Coatings*, vol. 10, no. 4. MDPI AG, Apr. 01, 2020. doi: 10.3390/coatings10040333.

[10] S. Saleemi *et al.*, “Surface functionalization of cotton and pc fabrics using SiO2 and ZnO nanoparticles for durable flame retardant properties,” *Coatings*, vol. 10, no. 2, Feb. 2020, doi: 10.3390/coatings10020124.

[11] B. Kementerian Pertanian, “Kegiatan Lokakarya Penyusunan Roadmap Rami,” http://balittas.litbang.pertanian.go.id/index.php/id/tentang-kami/58-berita/1494-kegiatan-lokakarya-penyusunan-roadmap-rami.

[12] U. Abay, “Litbang Pertanian Hasilkan Nanobiosilika Dari Sekam Padi,” https://www.swadayaonline.com/artikel/170/Litbang-Pertanian-Hasilkan-NBS-Dari-Sekam-Padi/.

[13] S. Yuliani, T. Hidayat, K. Wahyuningsih, and Hoerudin, “Surface Modification of Nano-Biosilica Extracted from Rice Husk using A Silane Coupling Agent,” *IOP Conf Ser Earth Environ Sci*, vol. 752, no. 1, p. 012053, Apr. 2021, doi: 10.1088/1755-1315/752/1/012053.

[14] N. Setyawan, Hoerudin, A. Wulanawati, and Suismono, “Yield and properties of nanobiosilica extracted from rice husk using technical grade chemicals: effect of extraction temperatures and times,” *IOP Conf Ser Earth Environ Sci*, vol. 752, no. 1, p. 012036, Apr. 2021, doi: 10.1088/1755-1315/752/1/012036.

[15] A. Chandra, Y. I. P. A. Miryanti, L. B. Widjaja, and A. Pramudita, “Isolasi Dan Karakterisasi Silika Dari Sekam Padi,” *Jurnal Fisika dan Aplikasinya*, p. 200, 2016.

[16] Kartick K. Kartick, Santanu Basak, and S. K. Chattopadhyay, “Sustainable Flame-Retardant Finishing of Textiles: Advancement in Technology,” in *Handbook of Sustainable Apparel Production*, CRC Press, 2015, pp. 66–91. doi: 10.1201/b18428-7.

[17] M. Norouzi, Y. Zare, and P. Kiany, “Nanoparticles as effective flame retardants for natural and synthetic textile polymers: Application, mechanism, and optimization,” *Polymer Reviews*, vol. 55, no. 3, pp. 531–560, Jul. 2015, doi: 10.1080/15583724.2014.980427.

[18] “Review agricultural wastes as a source of silica material”.

[19] D. Stawski, “Application of layer-by-layer method for textiles,” in *Textiles: Types, Uses and Production Methods*, Nova Science Publishers, Inc., 2012, pp. 507–518.

[20] J. J. Richardson, J. Cui, M. Björnmalm, J. A. Braunger, H. Ejima, and F. Caruso, “Innovation in Layer-by-Layer Assembly,” *Chemical Reviews*, vol. 116, no. 23. American Chemical Society, pp. 14828–14867, Dec. 14, 2016. doi: 10.1021/acs.chemrev.6b00627.

[21] T. Kashiwagi, J. W. Gilman, K. M. Butler, R. H. Harris, J. R. Shields, and A. Asano, “Flame retardant mechanism of silica gel/silica,” *Fire Mater*, vol. 24, no. 6, pp. 277–289, Nov. 2000, doi: 10.1002/1099-1018(200011/12)24:6<277::AID-FAM746>3.0.CO;2-A.

[22] N. Attia, H. Ahmed, D. Yehia, M. Hassan, and Y. Zaddin, “Novel synthesis of nanoparticles-based back coating flame-retardant materials for historic textile fabrics conservation,” *Journal of Industrial Textiles*, vol. 46, no. 6, pp. 1379–1392, Feb. 2017, doi: 10.1177/1528083715619957.

[23] M. Przybylak, H. Maciejewski, and A. Dutkiewicz, “Preparation of highly hydrophobic cotton fabrics by modification with bifunctional silsesquioxanes in the sol-gel process.,” in *Appl. Surf. Sci.*, vol. 387, 2016, pp. 163–174.

[24] A. Putri, “Modifikasi Permukaan Kain Kapas untuk Penyempurnaan Superhidrofobik yang Ramah Lingkungan Menggunakan NBS dari Sekam Padi dan Carnauba Wax dengan Metode Layer-by-Layer,” Politeknik STTT Bandung, 2021.

[25] M. Karthigairajan *et al.*, “Effect of Silane-Treated Rice Husk Derived Biosilica on Visco-Elastic, Thermal Conductivity and Hydrophobicity Behavior of Epoxy Biocomposite Coating for Air-Duct Application,” *Silicon*, vol. 13, no. 12, pp. 4421–4430, Dec. 2021, doi: 10.1007/s12633-020-00772-z.

[26] S. Kristianingrum, “Handout Spektroskopi Infra Merah,” *Susila*, 2016.

[27] A. Abdullah and A. Mohammed, “Scanning Electron Microscopy (SEM): A Review Scanning Electron Microscopy (SEM): A Review,” *Proceedings of 2018 International Conference on Hydraulics and Pneumatics - HERVEX*, pp. 77–85, 2019.

[28] J. Alongi, A. Frache, G. Malucelli, and G. Camino, “Multi-component flame retardant coating techniques for textiles,” in *Handbook of Fire Resistant Textiles*, Elsevier Ltd, 2013, pp. 68–93. doi: 10.1533/9780857098931.1.68.