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Usage of UV-Curable Soybean Oil Based Coating Formulations for Pretreated Cotton Fabrics

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ABSTRACT

This study aims to design an alternative way for the laminated fabric manufacturing with a cleaner production method, by using a bio-based coating formulation and time/cost saving, environmentally friendly UV-curing technology, compared to the conventional petroleum based, heat and solvent requiring laminating process. For this purpose, acrylated epoxidized soybean oil oligomer was synthesized and included in coating formulations for the application on cotton fabrics via UV-curing. The obtained oligomer was characterized by FTIR and ^{1}H NMR spectroscopies. In order to enhance the bonding between the fabric and coating layer, fabrics were pretreated by sodium hydroxide, pectinase enzyme, and a commercial washing agent prior to the coating process. The effects of pretreatment methods on the wettability, tensile and peel strength, and abrasion resistance of the fabrics were all examined before/after coating process. Enzyme pretreatment revealed promising results by increasing the surface roughness, fibrillation, and hydrophilicity of the cotton fabrics. After coating and UV-curing process, the highest increment in tensile strength, the highest peel strength, and the least weight loss value against abrasion were all recorded in enzyme pretreated fabric.

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KEYWORDS

Soybean oil; cotton fabric; uv-curing; pectinase enzyme; peel test

1. INTRODUCTION

Nowadays the utilization of environmentally friendly, biodegradable, renewable materials in polymer manufacturing systems instead of conventional, petroleum based chemicals, is an important issue for both academicians and industry workers. Among all biodegradable resources, vegetable oils are important due to being universally available, non-volatile, non-toxic, non-depletable, cheap, and abundant. Vegetable oils consist of fatty acids/triglyceride molecules with different chain lengths, and number of double bonds. Fatty acids are the fundamental component of a vegetable oil that determine the chemical and physical properties of the oil. The unsaturation sites of the vegetable oil allow the chemical modification in order to be used as starting material in polymer synthesis. For instance, the major fatty acids of soybean oil are α-linolenic acid and linoleic acid have three and two double bonds on their backbone, enabling synthesis of different types of polymers, respectively.

Soybean oils are favored due to the being abundant, inherently biodegradable, having low toxicity, and presenting five different unsaturated sites. Epoxidation is the most preferred functionalization reaction of vegetable oils. The oxirane ring of the epoxidized soybean oil (ESBO) allows to the modification of oil with different chemical species, generally by acids, in further reactions. In literature, a number of researches have been made about the chemical modification of ESBO. Acrylated and methacrylated ESBOs have been used for various purposes such as oil-absorbing materials, alkyd modifiers, flame retardant coatings, 3D printing materials, printing inks etc. For instance, ESBO has been modified by methacrylic acid and vinyl phosphonic acid to obtain an organic-inorganic hybrid coating with flame resist property [1]. In another study, ESBO has been used to improve the wettability,

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biodegradation, and thermal properties of poly(vinyl alcohol) via the ring-opening reaction [2]. Soybean oil based methacrylates have been synthesized from ESBO as an alternative to the fossil-based resins and additives for the usage in stereolithography [3]. In another research, ESBO has been grafted on cellulose aerogels in order to enhance the absorbency and recyclability properties of aerogels for oil-absorbing materials [4]. In order to use the ESBO based oligomers in UV-curable formulations, the epoxide group of ESBO should be reacted by some chemical species contatining acrylate/vinyl functional groups such as acrylic acid, methacrylic acid, vinyl phosphonic acid etc.

Among all coating techniques, UV-curing technology is favored due to the formation of the crosslinked structure in just a few seconds resulting a time saving property, and requiring none or less solvent resulting an environmentally friendly manufacturing technique. Additionally, the crosslinking reaction of the coating formulation is performed at low temperatures resulting a cost saving property. The other advantages of UV-curing are high optical clarity, good adherence on various surfaces, high curing rates, high stability at storage, controlled elasticity, and high scratch resistance [5-14]. UV-curable soybean oil based oligomers have been searched for various purposes. For instance, ESBO has been reacted with hydroxyethyl methacrylated maleate in order to obtain UV-curable coating formulations with higher biomaterial content [15]. In order to obtain polymeric films with better thermal stabilities, UV-curable soybean oil based coating formulations have been reported with the reaction of ESBO and acrylic acid (AA), by the inclusion of a trifunctional acrylate monomer (trimethylolpropane trimethacrylate) as crosslinking agent [16]. UV-curable formulations with better coating performances have also been reported by the synthesis of acrylated ESBO and acrylated sucrose oligomers with high biorenewable contents [17]. Due to the excellent pigment wetting property, UV-curable acrylated epoxidized soybean oil (AESBO) formulations have been also used in lithographic printing inks [18]. The usage of UV-curable AESBO oligomers have also been accomplished in phase change materials for thermal energy storage [19], and in crack repair patch system for chemical reservoirs [20]. Whereas according to the literature review, no research has been found about their usage in the manufacturing of laminated cotton fabrics.

Laminated cotton fabrics are defined as multipurpose textile composites that are used as tent fabrics, truck covers, tarpaulin, tablecloths, raincoats, bibs, mats, bags etc. and must be durable against some specific usage conditions such as UV-light, flame, chemicals, water, heat, mold etc. In laminated fabrics, the reinforcing layer is generally a cotton fabric, whereas the matrix layer is made by non-degradable polymers such as polyvinyl chloride (PVC), polyurethane (PU), acrylic, high density polyethylene (HDPE), and ethylene vinyl acetate (EVA) [21, 22]. In a convetional lamination related previous study, acrylic based adhesive formulations have been employed in the lamination of cotton and polypropylene fabrics via knife coating method. The peel strength of these fabrics have been recorded in the range of 2.1-5.2 N [23]. In another study, polypropylene nonwoven fabrics have been laminated via knife coating method. The peel strength values have been found as 1.12-2.18 N for acrylic based and 4.2-12 N for polyurethane based adhesive formulations, respectively [24]. In order to enhance the performance of finishing and coating processes in textile industry, the hydrophobic impurities on fiber surface such as waxes, pectin, grease, hemicellulose, protein etc., should all be dissipated from the fiber. Therefore, textile surfaces need to be scoured by pretreatment methods in order to enhance the hydrophilicity and dyestuff uptake, to increase the bonding between the fiber/coating layer, and to improve the compatibility between fiber/finishing agent. In this study, an enzymatic washing process with pectinase enzyme, an alkali treatment with concentrated sodium hydroxide (NaOH) solution, and a commercial washing process with standard ECE washing agent were all employed as pretreatment methods. In textile industry, enzymes are used in various purposes such as scouring, bleaching, desizing, polishing, and denim abrading etc. Comparing to the other pretreatment methods, enzymatic washing steps present some superior properties such as being sustainable and eco-friendly, requiring less energy, and giving less deformation to the fiber surface. The alkali treatment on textile materials is used to improve the dye uptake, luster, appearance, dimensional stability, and drape. During the alkali treatment, the concentrated NaOH solution helps to dissolve the impurities such as lignin, hemicellulose, grease, and waxes on the fiber surface, resulting enhancement on absorbency due to the fibrillation. The ECE washing agent is a non-ionic, phosphated, without any optical brightening agent that is used in textile fastness tests by removing the water/detergent soluble impurities from the surface [25-29].

In this study, a light weight, bio-based laminated fabric was designed with a cleaner production method by using cotton fabric as reinforcing layer, AESBO as matrix layer, and UV-curing technology as coating method. For this purpose, ESBO was acrylated by AA then the obtained AESBO oligomers were included in coating formulations. AESBO oligomer was characterized by FTIR and ^{1}H NMR spectroscopies. In order to enhance the wettability of fabrics and to enhance the bonding mechanism between fabric and resin, cotton fabrics were pretreated by pectinase enzyme, NaOH, and ECE washing agent prior to the coating process. Coating formulations were applied on pretreated cotton fabrics and then cured by UV-light. SEM was employed to observe the effect of pretreatment methods on the fabric surface. Spray and absorbency tests were used to evaluate the wettability character of the fabrics after pretreatment methods. The abrasion and tensile properties of pretreated and coated UV-cured fabrics were investigated. Furthermore, the adhesion strength between the coated UV-cured fabric layers were also examined by means of peel test.

2. MATERIAL AND METHOD

2.1 Material

ESBO (MW=952 g/mole, EEW=232 g/equiv.), acrylic acid (AA), 1.6-hexanediol diacrylate (HDDA, reactive diluent), sodium hydroxide (NaOH), triphenyl phosphine (TPP, catalyst), hydroquinone (HQ, inhibitor) were all purchased from Merck and used as received. 1-hydroxycyclohexyl phenyl ketone (Irgacure® 184, photo initiator) was obtained from Ciba Specialty Chemicals. Non-ionic wetting agent (Uniwett HGA) and pectinase enzyme (Scourzyme L Novozymes) were purchased from Alfa Chemistry. ECE phosphated washing powder without optical brightening agent was purchased from SDL Atlas Co. Cotton fabrics (135 g/m^2, 42 warp/cm, 30 weft/cm, plain weaved) desized, bleached, ready to dye were supplied from a local manufacturer.

2.2 Oligomer Synthesis

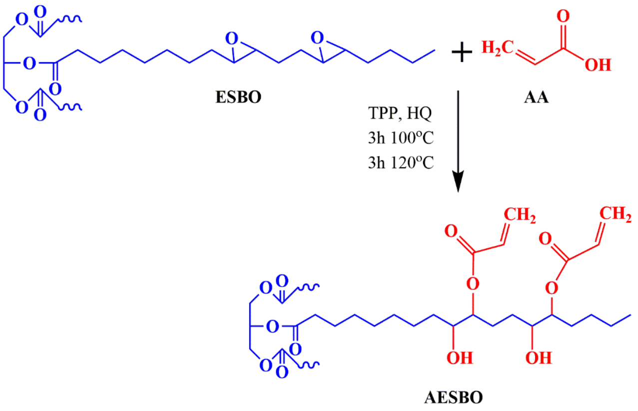
Synthesis of the AESBO was performed in a round-bottom flask, equipped with a nitrogen gas inlet, a condenser, and a magnetic stirrer. Considering the epoxy equivalent weight (EEW) of ESBO (232 g/equiv.), the ESBO:AA molar ratio was set as 1:5. The synthesis of the oligomer can be seen in Scheme 1. First, ESBO and HDDA (30% out of the total ESBO and AA amount) were loaded into the flask. 300 ppm HQ and 1000 ppm TPP were dissolved in AA in a beaker by using an ultrasonic bath. Then the AA solution was added dropwise to the main flask. The reaction was proceeded for 3 h at 100 oC, and for another 3 h at 120 oC until a constant acid value (AV) of 65.12 mg KOH/g was recorded. The epoxide ring opening reaction between the epoxide group of soybean oil and AA was initiated by the nucleophilic attack of the catalyst (TPP) resulting with the formation of phosphonium betaine. A proton of AA was attached to the betaine then an ester bonding was formed by the effect of carboxylate anion on the electrophilic carbon of the phosphorus [30].

2.3 Surface Pretreatments of Cotton Fabrics

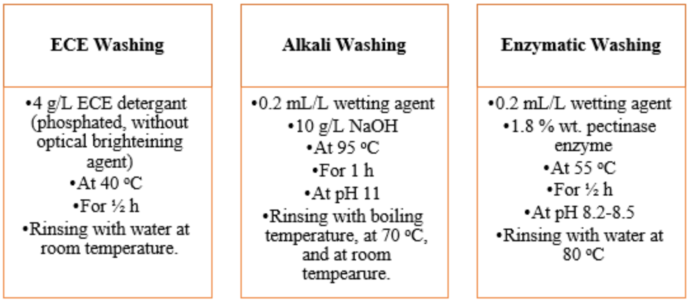
In order to enhance the wettability property of fabrics, and the adhesion between the fabric/coating layer, cotton fabrics were treated by ECE standard washing powder, concentrated NaOH solution, and pectinase enzyme prior to the UV-coating process. The fabric pre-treatment parameters are set according to our previous study [31] and given in Figure 1. Pectinase enzyme was chosen to decompose the pectinic impurities on cotton fabric. The parameters of ECE and enzymatic washing processes were set according to the manufacturer's commercial formula. Whereas the alkali treatment parameters were adjusted according to the previous studies about giving cotton more hydrophilic property by NaOH [25, 32, 33]. Wetting agent was included to the washing process in order to reduce the surface tension of water and to help spreading of drops on the fiber surface. Distilled water was used for each washing/rinsing processes. Cotton fabrics were cut in 15x20 cm dimensions allowing to perform various testing/analysis. Then fabrics were immersed into the washing bath on a Pyrex glass in 25 cm diameter, equipped with a magnetic stirrer. The pH in pectinase washing media was checked with care as the pH is very effective on the working mechanism of enzymes.

2.4 Application of the Coating Formulation

The conventional laminated fabric manufacturing requires the usage of excessive heat, water, and solvent whereas the coating process in this proposed method is performed at room temperature without the usage of water/excessive solvent. The schematic representation of the coating process can be seen in Figure 2. First, the pre-treated cotton fabrics were dipped into the bath containing the AESBO oligomer and 3 % wt. photo initiator. After 3 min dipping time, the excess resin was dissipated by placing the fabric between two PE films and pressing it with a squeezing roller in 500 g weight by hand. In order to prevent the oxygen inhibition during the UV-curing process, fabrics were put between two glass plates and were exposed to UV-light for 3 min from both sides of the fabric at room temperature. During the UV-curing stage of double layered fabrics, the glass plates also helps to keep the fabric layers tightly together to prevent any slippage. These dip-coating steps were applied on both single and double layered fabrics to perform the targeted tests and analysis. The weight of the cotton fabrics was recorded as around 170 g/m^2 that means a 25 % weight increment was observed after coating and UV-curing process.



Scheme 1. Synthesis of AESBO oligomer.



ECE Washing	Alkali Washing	Enzymatic Washing
•4 g/L ECE detergant (phosphated, without optical brighteining agent) •At 40 °C •For ½ h •Rinsing with water at room temperature.	•0.2 mL/L wetting agent •10 g/L NaOH •At 95 °C •For 1 h •At pH 11 •Rinsing with boiling temperature, at 70 °C, and at room tempearure.	•0.2 mL/L wetting agent •1.8 % wt. pectinase enzyme •At 55 °C •For ½ h •At pH 8.2-8.5 •Rinsing with water at 80 °C

Figure 1. Surface treatment parameters for each pre-treatment method.

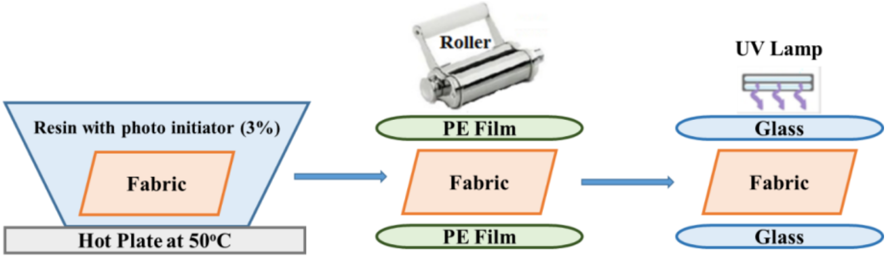


Figure 2. Schematic representation of the fabric coating and UV-curing steps.

2.5 Characterization

During the oligomer synthesis, the depletion of AA and epoxide groups were followed periodically with the help of titration methods according to the ASTM standards by means of AV [34] and EEW [35] measurements. The Fourier transform infrared (FTIR) spectra was recorded with a Perkin Elmer Spectrum-100 ATR FTIR spectrophotometer. The proton nuclear magnetic resonance (^{1}H NMR) spectra of the oligomer was obtained on Bruker AMX 500 MHz NMR instrument, in the solvent of dimethyl sulfoxide (DMSO) by using the internal reference of the tetramethylsilane (TMS). Physicochemical properties of the UV-cured free films were investigated in terms of degree of swelling (DS), gel fraction (GF), and weight loss against chemical reagents, respectively. All these tests were performed by dipping the free film particle into the solvent/solution at room temperature for one week. Toluene, ethanol, distilled water, and THF were all used as solvents for the DS and GF tests, respectively [36]. In order to measure the weight loss with chemical exposure, 10% hydrochloric acid (HCl), and 10% sodium hydroxide (NaOH) solutions were employed [37]. The morphological properties of fabrics after each surface treatments were investigated by using scanning electron microscopy (SEM, ZEISS® EVO MA 10 model). The wettability property of the pretreated cotton fabrics before and after coating process were evaluated by the absorbency test [36] based on the disappearance time of a water droplet on the surface that is recorded by a chronometer according to the AATCC-79 standard and the spray test [39] using a spray testing instrument with 45° slope according to the AATCC-22 standard. Tensile testing and peel test were both performed by using Instron 4411 tensile testing machine. In tensile test, the tensile strength and elongation values of pretreated fabrics with and without coating layer were measured [40]. The peel test [41] was used to investigate the adhesion property between the fabric and coating layer from the double-layered coated fabrics. The abrasion test was applied on pretreated fabrics with [42] and without [43] coating layer by using a Martindale pilling and abrasion instrument.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Oligomer

The aim of this study was to design a bio-based laminated fabric by using UV-curable coating formulations with an enhanced adhesion strength between the matrix and reinforcing layers. For this purpose, ESBO was modified with AA in order to obtain UV-sensitive functional groups in the oligomer structure. During the oligomer synthesis, the depletion of AA and epoxide groups was followed by titration methods, and given as AV and EEW. The obtained AESBO oligomer was also characterized by FTIR and ^{1}H NMR spectroscopies. EEW gives the weight of resin in grams which contains a 1 g equivalent of an epoxy group, whereas the AV illustrates the potassium hydroxide amount in milligram requiring to neutralize a 1 g of the oligomer [44]. The changes in AV and EEW during the reaction can be observed in Figure 3. Accordingly, the AV was gradually decreased due to the esterification reaction whereas the epoxide groups of soybean oil were depleted by the AA via epoxide ring opening mechanism. The reaction was ended after 6 h when a constant AV and EEW results were observed. As the epoxide concentration decreases EEW value increases. Thus, the highest EEW value and the least AV were recorded as 1,055 g/equiv. and 65 mg KOH/g, respectively.

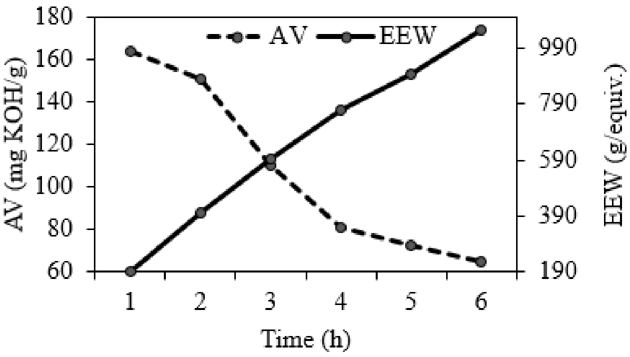


Figure 3. Changes in AV and EEW during the reaction.

The FTIR spectra of ESBO and AESBO oligomers were shown in Figure 4. The peak at 1744 cm^{-1} belongs to the carbonyl group of soybean oil. The C-H asymmetric stretching vibration peaks in $–CH_2$- and $–CH_3$ groups were observed at 2924 cm^{-1} and 2854 cm^{-1}, respectively. In the spectra of ESBO, the C-O-C asymmetric stretching vibration peaks at 823 cm^{-1} and 1155 cm^{-1} were attributed to the existence of epoxide group. These peaks were both disappeared after the reaction with AA. The newly formed peaks at 1619 cm^{-1} and 1636 cm^{-1} in AESBO spectra confirmed the existence of acrylate functionality with C=C double bond stretching vibration and C=O vibration. Additionally, the hydroxyl peak at 3474 cm^{-1} and C-H bending vibration peak at 809 cm^{-1} also support the epoxide ring opening reaction [45].

The reaction between the AA and epoxide groups of soybean oil can be confirmed by the ^{1}H NMR spectra. Figure 5 illustrates the ^{1}H NMR spectra of the AESBO oligomer with the assignation of the proton peaks. Accordingly, the peaks at 5.6-6.5 ppm region belong to the C=C structure of the acrylate functionality. The peaks at 1.1-1.4 ppm region are the protons of saturated triglyceryl backbone. The methylene protons of adjacent epoxy groups were observed at 1.4-1.7 ppm region. The characteristic methane and methylene proton peaks of the triglyceride backbone were appeared at 4.1-4.4 ppm and 5.1-5.3 ppm regions, respectively. The peak at 2.4 ppm is due to the protons in allylic positions. The methylene protons of the epoxide peaks at 3.6-3.8 ppm and the hydroxyl group proton peaks at 4.9-5.0 ppm regions confirm the epoxide ring opening reaction [15, 46].

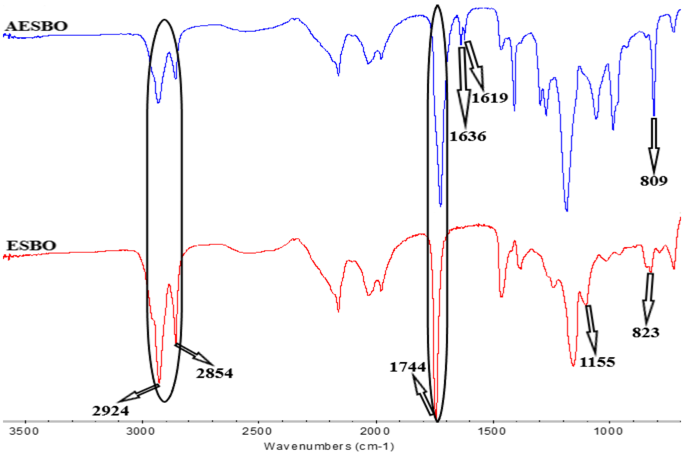


Figure 4. FTIR spectra of ESBO and AESBO oligomers.

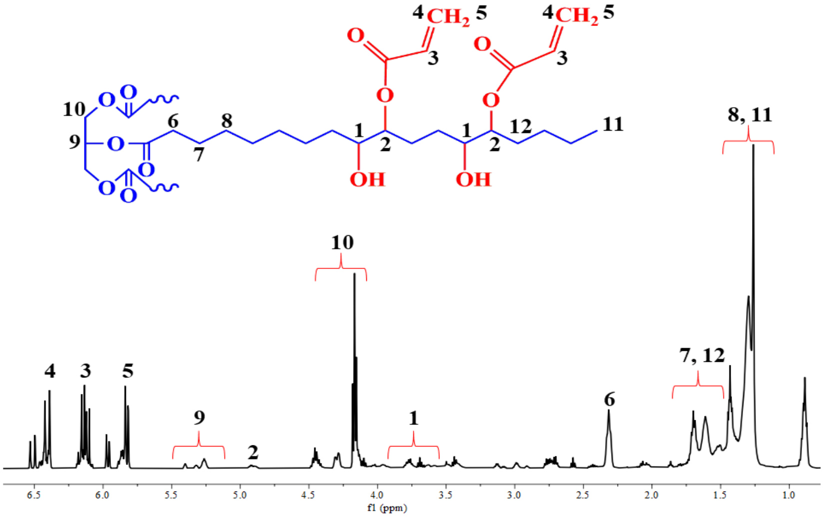


Figure 5. ^{1}H NMR spectra of AESBO oligomer.

3.2 Physicochemical Properties

The DS (%), GF (%), and weight loss (%) with chemical exposure values of the UV-cured free films and laminated fabrics in terms of each pretreatment method were all given in Table 1. The crosslinking density of polymeric structures is the key factor determining the physicochemical properties. The DS (%) and chemical resistance weight loss (%) values decrease with increasing crosslinking density. Whereas higher crosslinking densities are attributed to the higher GF (%) values. Accordingly, the GF values of raw fabric and fabrics with each treatment method were recorded as 100. This result can be explained by the lack of any extractable impurity on cotton fabric surfaces. Due to the highly cross-linked structure the highest GF value of 98.88% was recorded in UV-cured free film. The GF value of the UV-cured oligomer was slightly decreased after the application on fabric surfaces. Considering the treatment methods, the GF values were found in the following order: enzyme > ECE > NaOH. A remarkable decrease in GF value of coated raw fabric was observed. That may be incompatibility between the raw fabric and coating layer. After the surface treatment methods, a better cross-linked oligomer structure can be occurred between the fabric and coating layer thus the GF values were increased.

In order to observe the swelling properties of the samples ethanol, water, and toluene were chosen as solvents since they are not reactive at room temperature and may have only weak physical interactions with the sample. The swelling property is mainly related to the affinity between the sample and solvent, and the polarity of the solvent. Water and ethanol are strongly polar solvents whereas toluene shows slightly polarity [47]. Accordingly, due to the affinity between the hydroxyl groups of cotton fabric and polar solvents, the DS values were found as follows: water > ethanol > toluene in fabrics without coating layer. After the application of the coating layer, the DS values for each solvent by means of the treatment method were found in the following order: NaOH > ECE > enzyme. Considering the coated fabrics, the highest swelling values were observed in coated raw fabric due to the existence of impurities on fiber surface that inhibit a complete adherence of coating layer to the fiber surface.

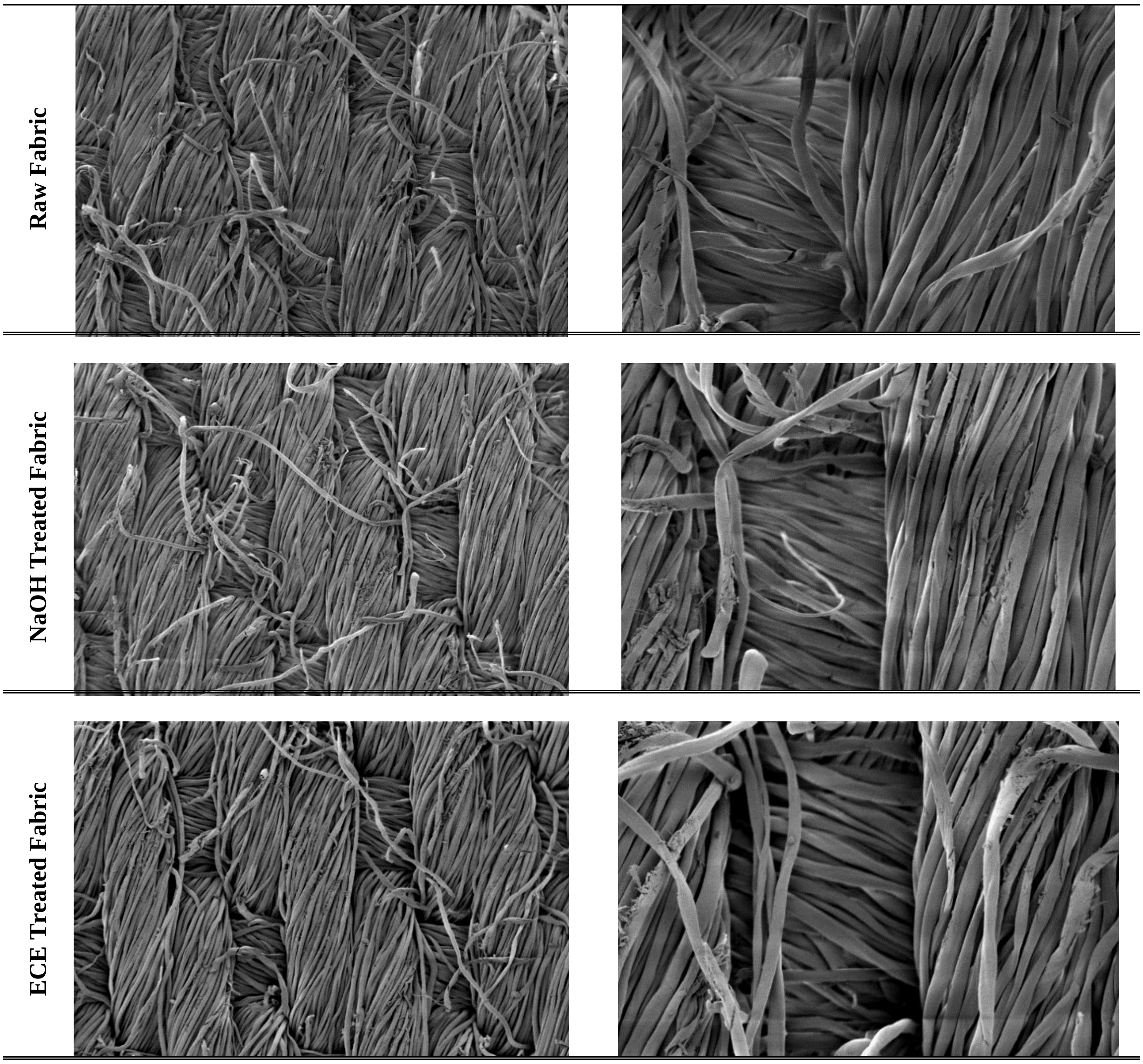
The weight loss values of the UV-cured free film and coated fabrics in NaOH (10%) solution is greater than in HCl (10%) solution. This result can be expressed by the basic hydrolysis of the ester groups in the oligomer which is initiated by the attack of the hydroxyl ion on the carbonyl carbon resulting the formation of tetrahedral intermediate that collapses immediately and gives the sodium carboxylate salt in NaOH solution. Whereas the ester groups are more stable in HCl solution and only partially protonated because the acidic hydrolysis is reversible like esterification reaction and does not go to completion. Considering the fabrics without coating layer, the weight loss value in HCl solution is greater than in NaOH solution. This result can be supported by the durability of glycoside bonds of cellulose in alkaline environment. The hydrolysis of cellulose is occurred via the cleavage of glycoside bonds in the presence of acids. After the application of coating layer, the weight loss values for both chemical solution were recorded as follows: NaOH > ECE > enzyme [48-50]. Considering the overall physicochemical results, due to the highest fibrillation and scouring performance of enzyme treated fabric, the coating layer was adhered best to this sample. Thus the least DS and chemical resistance weight loss values with the highest GF value were all obtained in that sample.

3.3 SEM Images

The surface morphology of the pre-treated fabric samples without coating layer was observed by means of SEM. Figure 6 shows the SEM images of raw fabric and fabrics with each pre-treatment methods in various magnifications. Accordingly, a smooth and uniform fibrillar orientation was observed in the SEM images of raw fabric. The uniformity of the fibrillar orientation was partially destroyed by the pre-treatment methods. The fibrillation can be best observed in the SEM image of enzyme treated fabric in 600 magnification. Fibrils became apart from each other that means much more surface area was created allowing to the more resin penetration. Besides the fibrillation phenomenon, fibers gained a rougher look after pre-treatment methods due to the dissipation of the impurities via the abrasive/cleaning effects of NaOH solution, ECE detergent, and pectinase enzyme.

Table 1. Physicochemical properties of UV-cured free film and fabrics with each treatment method with/without coating layer.

Samples	DS (%)			GF (%)	Chemical resistance weight loss (%)	
	Toluene	Ethanol	Water		NaOH (10%)	HCl (10%)
UV-cured free film	6.47	11.93	16.21	98.88	14.42	4.92
Raw fabric	0	1.79	15.28	100	3.02	5.93
Coated raw fabric	3.92	4.03	4.39	89.91	12.28	1.92
NaOH treated fabric	0	2.13	19.35	100	1.79	4.18
Coated, NaOH treated fabric	2.16	2.54	3.78	94.59	11.06	1.21
ECE treated fabric	0	2.86	27.27	100	1.65	4.24
Coated, ECE treated fabric	1.43	2.01	3.01	98.27	10.52	0.46
Enzyme treated fabric	0	4.17	30.77	100	0.33	2.49
Coated, enzyme treated fabric	1.16	1.32	2.74	98.32	8.73	0.31



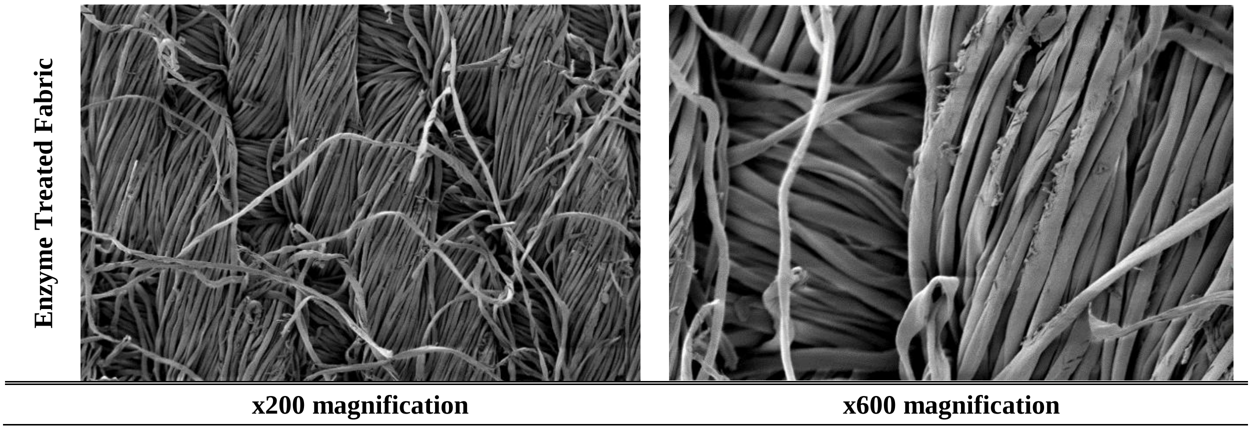


Figure 6. SEM images of raw fabric and fabrics after pre-treatment methods.

3.4 Wettability Properties

The wettability properties of fabrics for each pretreatment method before and after coating process were investigated by means of absorbency test and spray test according to the AATCC-79 [38] and AATCC-22 [39] standards, respectively. The absorbency test value illustrates the disappearance time of a water droplet on the fabric surface that is measured by a chronometer. In the spray test, the specimen was placed with a 45o slope on a spray testing instrument and was wetted by a certain amount of distilled water in a certain time period. The evaluation is made by comparing the wetted surface with the standard images. Results are given in the range of 0-100. Zero refers to a highly hydrophilic behavior whereas 100 means no wetting observed on the surface. Figure 7 shows the spray and absorbency test results of raw fabric and fabrics after the application of pretreatment methods without the coating layer. The spray test result of raw fabric was recorded as 50 that means the specimen was only wetted through the spray points. After pre-treatment processes, the spray test results were recorded as 40 (NaOH treated), 20 (ECE treated), and 0 (enzyme treated), respectively. This result proves the enhancement in wettability character of fabrics via pre-treatment methods. The enhancement in hydrophilicity was mainly based on the increased fibrillation with a more surface area for the connection of water molecules with fiber surface. The spray test results of fabrics after coating and UV-curing process were recorded as 100 for each sample due to the highly hydrophobic nature of the surface. Considering the absorbency test, the disappearance time of water droplet on the fabric surface decreased after the application of pre-treatment methods due to the fibrillation. The absorbency test results were found as 28 s (raw fabric), 7 s (NaOH treated), 5 s (ECE treated), and 3 s (enzyme treated). The spray and absorbency tests showed both consistent results supporting that the best hydrophilic nature was found in the enzyme treated fabric sample. The absorbency test was also applied on fabrics after coating and UV-curing process. The water droplet stayed more than 24 hours on the surface for each sample indicating that a hydrophobic character was observed due to the presence of the coating layer on the fabric surface.

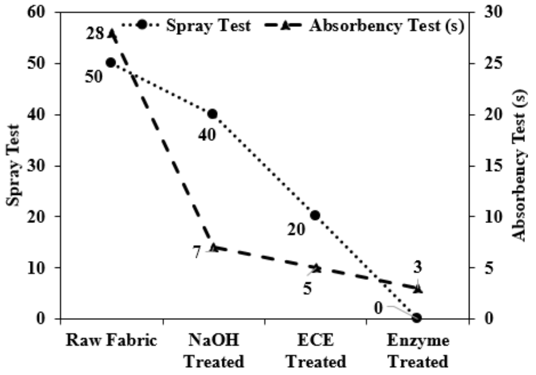


Figure 7. Wettability test results of raw fabric and fabrics after pre-treatment methods.

3.5 Tensile and Peel Test

The tensile and peel strength values of fabrics before and after coating process with each pre-treatment method were all shown in Table 2, and the image of enzyme treated double-layered coated UV-cured fabric sample after peel test was illustrated in Figure 8. The tensile strength values of fabrics without coating layer were all decreased for each pre-treatment method due to the dissipation of the impurities with the cleaning and etching effects of the detergent, NaOH solution, and pectinase enzyme [51]. The highest tensile strength loss was observed in alkali pre-treated fabric. This result is stemming from the abrasive effect of alkaline media via the removal of the hemicelluloses and other non-cellulosic impurities [52]. In order to see the effect of coating layer to the tensile strength raw fabric and pre-treated fabrics were coated as single-layered. Accordingly, the coating layer helped to increase the tensile strength for each sample. The increment in tensile strength was recorded in the following order: enzyme>ECE>NaOH. Due to the best fibrillation performance of enzyme treatment, the coating layer was well penetrated on the fiber surface thus the highest tensile strength value of 1102 N was recorded in the enzyme treated fabric. For some specific applications, laminated fabrics were manufactured as double-layered for the enhanced tensile properties and durability. In order to investigate the adhesion property in double-layered laminated samples, peel test was employed. The peel strength values were all increased after the application of pre-treatment methods due to the fibrillation and increment in surface roughness that strengthens the adhesion forces between the fiber and the coating layer. The highest peel strength value of 23.6 N was recorded in the enzyme treated double-layered coated UV-cured fabric due to the highest fibrillation performance of enzyme treatment resulting a better coating formulation absorbance by the fibers. As can be seen in Figure 8, the peeling was observed between the fabric layers without any deterioration on the fabric surface/shape. The schematic representation of the bonding mechanism between the fabric and the coating layer can be observed in Figure 9.

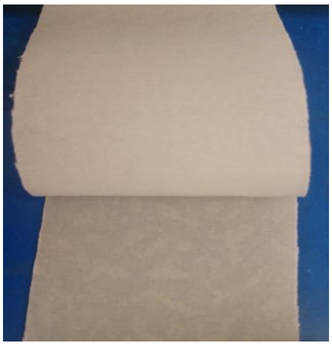


Figure 8. Image of the enzyme treated double-layered coated UV-cured fabric sample after peel test.

Table 2. The tensile and peel strength values of fabrics before coating and after single/double-layered coating processes.

	Raw fabric	**NaOH treated**	**ECE treated**	**Enzyme treated**	
Tensile strength (N)	**827**	**514**	**756**	**790**	**Uncoated**
	862	**617**	**988**	**1102**	**Single-layered coated**
Peel strength (N)	**17.6**	**18.3**	**19.9**	**23.6**	**Double-layered coated**

3.6 Abrasion Test

The abrasion resistance values of raw fabric and fabrics with each pre-treatment methods, with and without coating layer were all given in Table 3. The used abrasive surface changes with regard to the fabric surface property, that means if there is no polymeric coating layer on the fabric surface the abrasive material should be a 100% wool fabric. Whereas if the fabric was coated by a polymeric material the abrasive surface should be a sandpaper. In order to perform the abrasion resistance test, fabrics were cut in 5 cm diameter and allowed to be abraded by a standard wool fabric for fabrics without coating layer [43], and by a sandpaper for fabrics with coating layer [42]. In the abrasion resistance test of fabrics without coating layer, the test was ended when a yarn break is observed in both warp and weft directions and results were given in terms of "cycle". Whereas the weight loss after 100 cycle abrasion was recorded in abrasion resistance test of fabrics with coating layer and results were given as weight loss percentage. Accordingly, the abrasion resistance of raw fabric was recorded as 49,000 cycle. After the application of pre-treatments, the abrasion resistance values were all decreased and recorded as 45,000 cycle (NaOH treated), 43,000 cycle (ECE treated), and 38,000 cycle (enzyme treated), respectively. This result can be explained by the increment in fibrillation and surface roughness on the fabric surface. The abrasion resistivity of smooth surfaces is greater than the rough surfaces [53]. After coating process, the raw fabric showed a 6.05 % weight loss against abrasion. When the fabrics were pre-treated prior to the coating process, the weight loss percentages against abrasion were all decreased. Due to the increment in surface area via fibrillation and enhancement in surface roughness, a better penetration and adherence of the coating layer were all accomplished [54]. Thus a better bonding occurred between the fiber and the coating layer. The least weight loss value against abrasion was recorded as 2.81 % in enzyme treated fabric sample.

The possible bonding mechanism of double layered cotton fabric can be observed in Figure 9. The hydroxyl groups are responsible for the bonding mechanism which exist inherently on cotton fabric and occur in AESBO oligomer via ring opening reaction. Besides, the hydroxyl groups in AESBO oligomer give polarity to the coating layer resulting a better wettability character which helps to adhere cotton fabric [54, 55]. Accordingly, strong hydrogen bonding is formed between the hydroxyl groups of cotton fabric; carbonyl groups of acrylate, carbonyl groups of triglycerides, and hydroxyl groups of AESBO oligomer.

Table 3. Abrasion resistance results of the fabrics before/after coating process.

Abrasion resistance	**Raw fabric**	**NaOH treated**	**ECE treated**	**Enzyme treated**	
Cycle	**49,000**	**45,000**	**43,000**	**38,000**	**Uncoated**
Weight loss (%)	**6.05**	**5.54**	**3.77**	**2.81**	**Coated**

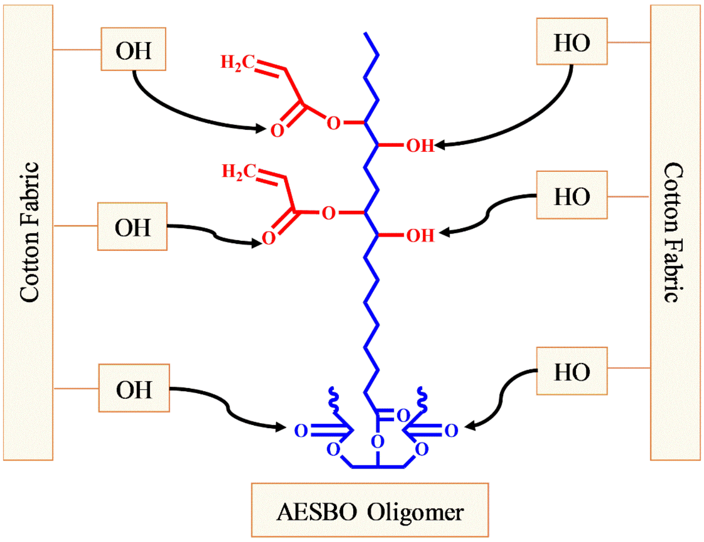


Figure 9. The bonding mechanism between the cotton fabric and the coating layer.

4. CONCLUSION

The manufacturing of a bio-based laminated fabric via environmentally friendly UV-curing technology was aimed by using cotton fabric and soybean oil based oligomer. ESBO was reacted with AA in order to obtain the UV-curable AESBO oligomer. FTIR and ^{1}H NMR spectroscopies prove the existence of acrylate groups on soybean oil structure and the newly formed hydroxyl groups via ring opening reaction. Cotton fabrics were pretreated by NaOH solution, ECE detergent, and pectinase enzyme prior to the coating process to obtain a better bonding between the fabric and the coating layer by supplying roughness, fibrillation, and hydrophilic character to the fabric.

Among all pretreatment methods, enzyme pretreatment showed the best performance by increasing the surface roughness, fibrillation, and hydrophilicity of the cotton fabrics. This result was supported by the spray, absorbency, swelling, gel fraction tests, weight loss measurement against chemical exposure, and SEM images. The spray and absorbency test results of coated UV-cured fabrics were found as 100 and >24 hours, respectively. These results indicate a hydrophobic character was obtained after the application of the coating layer. The coated UV-cured fabrics were also examined in terms of tensile, peel, and abrasion properties. According to the overall results, the highest increment in tensile strength, the highest peel strength, and the least weight loss value against abrasion were all recorded in enzyme pretreated fabric. As mentioned in Introduction section, in conventional acrylic based lamination related studies, the peel strength values have been found in the ranges of 1.12-12 N. In the present study, a remarkable enhancement was achieved in enzyme treated double layered fabric sample with a peel strength value of 23.6 N. In summary, bio-based, hydrophobic, laminated UV-cured cotton fabrics with enhanced tensile properties were designed with a cleaner manufacturing route compared to the conventional laminating industry. Future studies are in the way of coloration, and giving flame resistance and thermal insulating properties to the proposed laminated fabrics.

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