Bulgarian Chemical Communications, Volume 49, Special Issue L (pp. 79 – 85) 2017

The effect of ultrasound treatment on soy protein and chitosan coating solution for packaging paper

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Submitted October 20, 2016 ; Accepted February 12, 2017

From the presented research, bio-based polymers (soy protein and chitosan) were used as coatings on packaging paper. Ultrasound treatment was used for the preparation of the coating solution. The coating solution was consisted from chitosan and soy protein in ratio 1:1. The goal of the research was to make a paper coating, which will be biodegradable, will have an improved mechanical and barrier (grease, water vapour transmission) properties. The focus of the use of ultrasound was meant to reduce the production costs and to make paper with better barrier properties, compared to uncoated and coated paper, which solution was not pre-treated. The tensile properties (tensile stress and strain) of pre-treated, solution-coated paper have improved. Due to protein addition in the coating, the strength and toughness of the paper (pre-treated and not pre-treated solution), compared to uncoated enhanced. Furthermore, the surface of treated, coated paper was more even, without many defects, pinholes or cracks. It was observed that the surface of untreated, coated paper is less smooth. The results have shown that grease migration was detected, bur very small amount of the stained percent area of untreated and coated paper was detected, about 1%. The detected stained percent area for ultrasound treated coated paper was less, about 0.5%. The results have shown that coating without ultrasound treatment is acceptable, but with ultrasound treatment, the properties of packaging paper have improved even more.

Key words: ultrasound treatment, soy protein, chitosan, grease, tensile properties

INTRODUCTION

Recently, bio based polymers are very popular in different fields of materials science. The annual worldwide paper and board production is more than 370 million tons, where 40 % of these refer to paper and board for packaging [1]. Special attention should be given in the field of packaging, since the use of these polymers is important due to influence on the packed material. Natural polymers are already used as barrier coatings on packaging materials and in recent years, there has been a focus on renewable polymers, mostly as edible films and coatings [2-4]. Bio based coatings, such as starch (rice, corn, potato etc.), proteins (soybean etc.), polysaccharides (chitosan and chitin) and lipids are extracted directly from the biomass. Their advantage is that they are non-toxic, environmentally friendly and have great grease, gas and aroma barrier properties [3, 4].

Isolated soy proteins (ISP) have great film-forming property and are most commonly used as edible wraps for meat, vegetables etc. [5-9]. However, ISP is not expensive biopolymer, it's produced from extraction of soybean oil and it is compatible with commonly used packaging material polyethylene [10]. Chitosan, a polysaccharide, which is derived from crustacean chitin, is commonly used in the food packaging. Some studies have considered proteins and chitosan as coatings on paper [11-15]. In this study chitosan (CH) was also included as paper coating, because it is readily compatible with paper and has great antimicrobial and mechanical properties as coating material [13-15]. The main objective of producing blend coatings is to improve the permeability and mechanical properties according by the needs of applications. Many studies have been focused mostly on grease resistance, water permeability or improving mechanical properties of coated papers, but no attempts to develop coating using ultrasound treatment have previously been reported. Ultrasound is known as environmentally friendly process, used in many fields of materials science [16-17]. As it can be read in the literature, the positive effect of ultrasonic treatment on the starch dispersions and the application of ultrasonic treatment to starch films improves the moisture properties and provides stronger structure [18, 19].

The current study was thus conducted to investigate the possibility of improving paper coating solution using ultrasound as treatment technique.

EXPERIMENTAL

Materials

Kraft paper, with grammage 80 g/m^2, chitosan with molecular weight 20kDa (purchased from Sigma Aldrich, Austria), 98% malic acid (purchased

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from Sigma Aldrich, Austria), glycerol as plasticizer (purchased from Sigma Aldrich, Austria) and isolated soy protein (purchased from Sigma Aldrich, Austria) have been used in this study.

Preparation of blend coating solutions

Firstly solutions of each compound (chitosan and soy protein) have been prepared. The chitosan solution was prepared by dissolving 2g of chitosan in 100 ml of 98% malic acid. The solution was mixed at 90°C for 5 minutes until chitosan was not dispersed. Before cooling down, coating solution was filtered through a polyester screen (mesh no. 140 with mesh opening 160 µm), by aspiration to remove small lumps in the solution.

Separately soy protein solution was prepared by dissolving soy protein (5g) in distilled water (100 ml). The solution was kept at 85°C for 30 minutes and then in a water bath at 45°C for 2h [25]. After that it was pH-adjusted to 10±0.1 1N NaOH. Soy protein coating solution was also filtered through a polyester screen, to remove undissolved materials.

After that chitosan and soy protein solutions were mixed together and glycerol as plasticizer (40 % w/w of total solid weight in the solution) was added.

Ultrasound treatment of coating solutions

The blend solution was put into ultrasonic bath (Asonic, Ultrasonic bath, Slovenia) for 15 minutes, using constant 35 kHz frequency. After the ultrasound treatment, the solution was left in the bath for another 15 minutes.

Coatings on paper

After the solutions were prepared and treated with ultrasound, the coating with a coater proceeded. Kraft paper was coated with hand coater, at ambient temperature, using 120 µm blade. On each paper 5 g/m^2 was applied. The untreated and ultrasound treated solution coated papers were dried at 50°RH and 23°C.

ANALYSIS METHODS

Grammage and thickness

The grammage was determined in accordance with ISO 536 standard. Density and specific surface volume were calculated from the grammage and thickness, according to standard ISO 534. The thickness of sample papers was measured with a precision digital micrometre (Mitutoyo Corporation, Japan), to the nearest 0.0001 µm at 10 random locations on each paper.

Tensile properties

Tensile strength and elongation at break were determined on a tensile testing machine Instron 6022. The samples were analysed at standard atmosphere 23°C ± 1°C of temperature and 50% ± 2% of relative humidity. The cross speed head was 0.1 mm/s. Paper stripes of 18 cm in length and 1.5 in width were used. Ten probes of each sample in the machine direction (MC) and cross machine direction (CD) were tested.

Grease barrier properties

Grease resistance of paper coated with untreated and ultrasound treated blend solution of ISP and CH, was determined using a modified TAPPI test T-507, which was presented from Park et al. [10]. Smaller stained areas per hour on coated paper indicated greater grease resistance.

Water vapour properties

Thickness of the films has an influence on water vapor properties [20, 21]. Coatings from biopolymers have mostly hydrophilic nature and also the thickness of the coating influences on water barrier and mechanical properties. In our research thickness (mean values) of the coated papers were used in calculations for water vapour properties.

To determine WVP of the coated paper, the ASTM E96 standard method was used. To ensure the best results of the WVP, the silicone sealant was applied around the cup edge. Samples with exposed area of 50 cm^2 were tested at 90 ± 2% RH and 38 ± 2°C for 24 hours. The WVP was expressed in gram units, per square meter per day. Three samples per each paper sample were tested.

Surface

The SEM micrographs of coated paper surfaces were taken with a scanning electron microscope (JSM-6060 LV). The instrument operated at 10 kV and 1000X magnification.

RESULTS AND DISCUSSION

Basic paper properties

Grammage and thickness influence the physical, optical and water barriers. The thickness has an effect on stiffness of the paper. Table 1 presents determined properties of uncoated and coated paper (with and without ultrasound treatment of the solution).

It can be seen from Table 1 that on coated paper 5 g/m^2 of blend coating solution was applied onto the surface of the paper. As expected, the thickness increased and there are also changes in density and specific volume.

Table 1. Determination of grammage, thickness, density and specific volume of uncoated, coated and coated-ultrasound treated paper

Sample	Grammage [g/m^2]	Thickness [μm]	Density [g/m^3]	Specific volume [m^3/g]
Uncoated	80	122	655.74	0.00153
Coated	85	132	644.94	0.00155
Coated-treated	85	130	653.85	0.00153

Mechanical properties

Tensile properties such as tensile strength and elongation are very important for packaging materials. With coating, tensile properties can be improved. Therefore it can be more flexible, stiff etc. The results of the effects of the coating are shown in Figure 1, where it can be seen that elasticity increased, but tensile strength decreased in both directions. Nevertheless, elongations at break were better at all coated samples. In general, the behaviour and properties of paper are less flexible in machine direction (MD) as in cross direction (CD). In CD direction papers are more extensible and stiff. It can be proved that coating improved elasticity of sample papers and even more at papers, which coating was pre-treated with ultrasound.

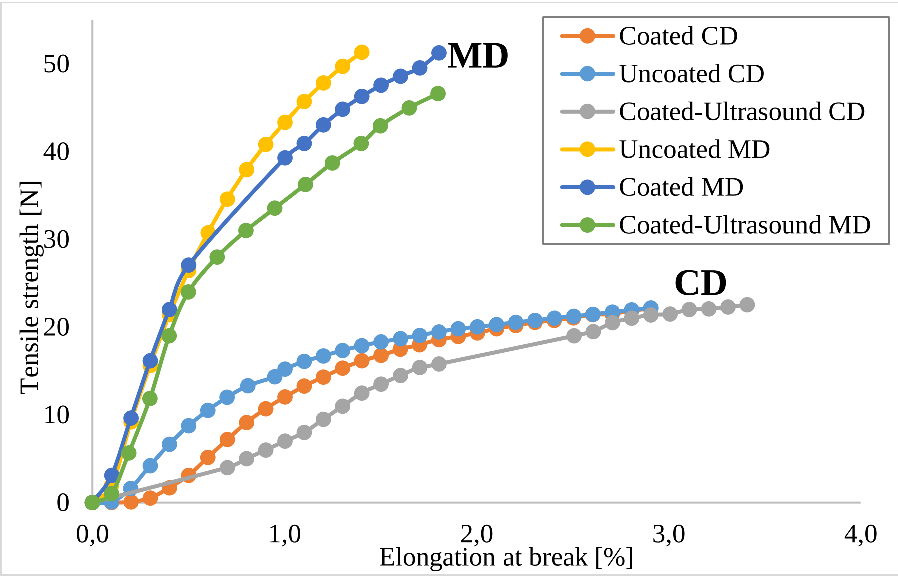

Figure 1. Tensile strength and elongation at break for uncoated, coated and coated-ultrasound treated paper in MD and CD directions

Grease barrier and water vapour properties

Grease barrier properties of analysed papers were affected by the coatings. In the first 1h the percent of stained area was at uncoated paper much higher than at both coated samples (Figure 2). The results of grease migration at coated samples are probably due to very small pinholes, cracks, where grease could permeate through the coating. After 5h of the test, the grease migration increased at uncoated paper (for 18 %), as well as at both coated papers. Still, there was less stained area detected at coated paper with ultrasound (6%), in comparison to coated sample (8%).

Defects on the coating surface might explain why the percent of stained area are still detected after 8 hours.

It is known that paper has certain grade of moisture, which depends on relative humidity, types of used pulp, degree of refining and types of used coatings. For packaging materials it is very important to have excellent barrier properties. One of them is also water vapour permeability (WVP). WVP is determined as the amount of water that permeates through the paper of certain thickness per unit time. From Figure 3 it can be seen that ultrasound treatment increased WVP barrier of coated paper, compared to coated, untreated or uncoated sample. The moisture at both coated samples decreased. Reducing of moisture was small, at coated paper moisture decreased for 0.6%% and coated, ultrasound treated for 1%. The influence of ultrasound led to improved surface distribution of the coating, where less pores were detected as well as cracks and other deformations. It was proved that such coating had denser structure, which also increased water vapour barrier. Thus, ultrasound treatment caused rearrangement of free mobile chains of the polymer matrix of the coating, which for that reason more homogeneous formation of the coating has been made. On moisture and WVP soy protein and chitosan as polymers had influence. Soy protein is known that it exhibits poor WVP properties due to its hydrophilic nature [22]. However, chitosan has hydrophobic nature, it is the only positively charged, naturally occurring polysaccharide [13]. Coatings in combination with chitosan and proteins can give effective water barriers with other prospective properties, which are important for packaging materials.

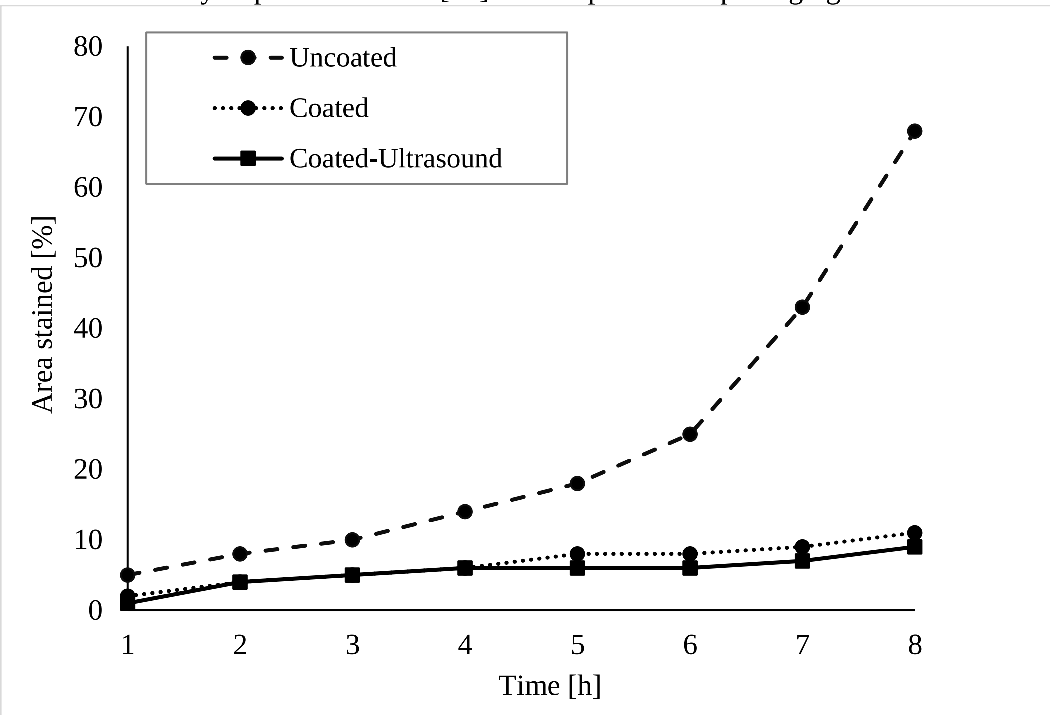

Figure 2. Grease permeation of uncoated, coated and coated-ultrasound treated paper.

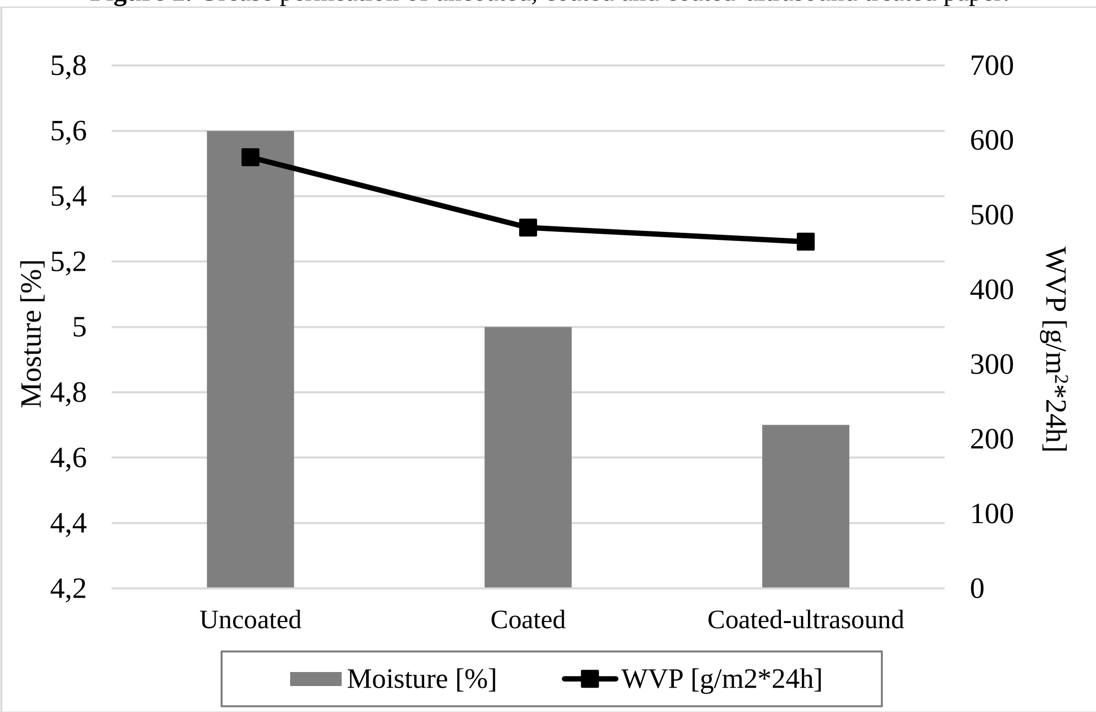

Figure 3. Moisture and water vapour permeability (WVP) of uncoated, coated and coated-ultrasound treated paper.

Surface

All micrographs show paper surface at 1000x magnification and are presented in Figure 4 (a-c). As expected, the surface of coated paper revealed smoother surface, compared to uncoated paper, which was also proven with other presented analysis in this paper. Even more can be seen at coated paper (Figure 4c), where coating solution was pre-treated with ultrasound.

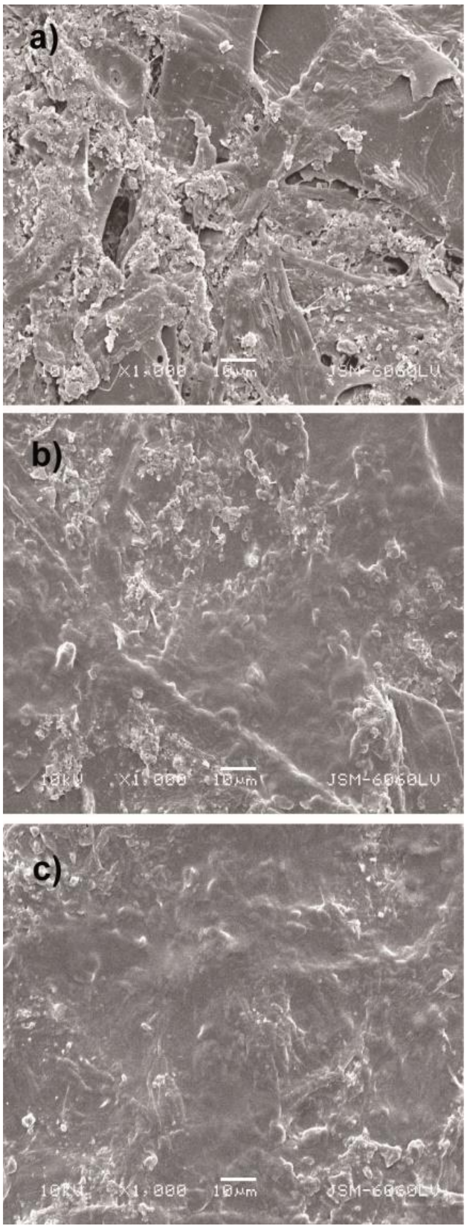

Figure 4. SEM micrographs of uncoated (a), coated (b) and pretreated coated (c) paper.

CONCLUSIONS

In recent years, various bio-based coatings for packaging materials have been developed, which have different barrier properties. Therefore the concept of coatings with biodegradable polymers represent stimulating route to create new packaging materials, with improved properties. Bio polymers used in our research are available in the market and their properties can help to improve the packaging paper. With ultrasound treatment we proved that it is effective procedure to improve coating solution and coating itself. In the literature, there are no reported studies of ultrasound treatment of soy protein and chitosan solution suitable as coating for packaging paper. Blend soy protein and chitosan coating possesses good grease and water vapour barrier properties and mechanical properties, which are useful for packaging materials. From the research it was proven that mentioned properties improved even more at solution, which was pre-treated with ultrasound.

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ЕФЕКТ НА УЛТРАЗВУКОВОТО ТРЕТИРАНЕ НА РАЗТВОРИ ОТ СОЕВ ПРОТЕИН И ХИТОЗАН, ПРЕДНАЗНАЧЕНИ ЗА ПОКРИТИЯ НА ОПАКОВЪЧНА ХАРТИЯ

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Постъпила на 20 октомври, 2016 г.; приета на 12 февруари, 2017 г.

(Резюме)

В настоящето изследване се използват полимери на биологична основа (соев протеин и хитозан) за покрития на опаковъчна хартия. Приложено е ултразвуково третиране за подготовка на полимерния разтвор. Този разтвор се състои от хитозан и соев протеин в отношение 1:1. Цел на изследването бе да се постигне биоразградимо покритие с подобрени механични и предпазни свойства (срещи масла, влага). Фокусът на ултразвуковото третиране бе в намаляването на производствените разходи и подобряването на защитните свойства спрямо хартия без покритие или с покритие без такова третиране. Свойствата на опън (напрежения и деформация) се подобряват при покрития с предварително третиране. Поради добавянето на протеин в покритието (с и без третиране) здравината и твърдостта на хартията се подобряват спрямо хартията без покритие. Освен това, повърхноста на третираната хартия е по-еднородна, без много дефекти, дупчици и пукнатини. Повърхността на не-покритата хартия е по-малко гладка. Резултатите показват, че е налице миграция на мазни петна, но повърхността им не превишава 1% при покрита и непокрита хартия. Когато разтворите са третирани с ултразвук, площта на петната е около 0.5%. Покритията без ултразвуково третиране са приемливи, но свойствата им се подобряват след такава обработка.