THE EFFECT OF PHYSICAL ADHESION PROMOTION TREATMENTS ON INTERFACIAL ADHESION IN CELLULOSE-EPOXY COMPOSITE

Sanna Siljander[1], Jani Lehmonen[2], Atsushi Tanaka[2], Jukka Ketoja[2], Pirjo Heikkilä[2], Matti Putkonen[2]
Johanna Lahti[1], Essi Sarlin[1], Jyrki Vuorinen[1]

[1]Tampere University of Technology, Department of Materials Science
P.O. Box, 33101 Tampere, Finland
Email: sanna.siljander@tut.fi, web page: http://www.tut.fi

VTT Technical Research Centre of Finland
P.O. Box, 1000, 02044 VTT, Finland
Email: jani.lehmonen@vtt.fi, web page: http://www.vtt.fi

Keywords: Adhesion promotion, interfacial adhesion, foam forming, cellulose-epoxy composite

ABSTRACT

The adhesion between reinforcing fibres and matrix material is crucial for the performance of composite structures. In this study we treated foam formed cellulose fibre sheets with plasma and atomic layer deposition (ALD) treatments to achieve better adhesion between cellulose fibres and epoxy matrix. Plasma treatment was done using 8 kW and 12 kW outputs and ALD cycles with Ti_2O and Al_2O_3. Surface treated foam formed sheets were laminated into composite structure with epoxy resin using vacuum assisted resin infusion. Complete laminated composites were water jet cut and interlaminar shear strength was measured. Effect of plasma treatment to adhesion was minimal and ALD treatment had minimal or no effect at all. Reason for low ILSS values can be explained with high void content of samples caused by processing aids in foam forming process.

1 INTRODUCTION

The performance and structure of fiber reinforced composites depends on the properties of the individual components such as matrix, fibers and their compatibility, adhesion and bonding [1][2]. Reinforcing fibers can be synthetic or natural; regardless of the origin of fibers the adhesion between fibers and matrix is crucial for performance of the composite structure.

The trend in the composite research and development is to produce eco-friendly composites. Cellulose fibers are used with both thermoplastic and thermosetting polymer matrix materials. The low thermal stability of natural fibers narrows the possible matrix material selection, since the processing temperature of thermoplastics and the curing temperature of thermosetting materials have to be less than 200 ^{o}C. Above this temperature natural fibers lose their mechanical properties and start to degrade [3][4].

Epoxy resins are the most typical thermosetting matrices in cellulose fiber reinforced composite structures. Some mechanical properties of the epoxy (EP) matrix are reported to increase after the addition of cellulose fibers, but limited compatibility between cellulose fibers and the epoxy matrix restrict wider usage [5].

Natural fibers have many possible characteristics for many engineering applications due to the low cost, non-toxic, very high strength to weight ratio, light weight, renewability, biodegradability and low wear to processing equipment. One major concern is the polarity of cellulose and high density of hydrogen bonds. This hydrophilicity causes high moisture absorption and weak adhesion to the hydrophobic polymer matrices [6][4]. To improve adhesion between natural fibers and polymeric matrices many physical and chemical treatments are used to overcome this incompatibility [7][5]. Chemical treatments have been used to enhance the interfacial adhesion between composite components but problem is that the treatments are costly, time consuming and chemicals have to be disposed safely afterwards. [1]

In this study, cost effective, clean and dry continuous process and relatively stable and uniform outcome were the reasons for selecting atmospheric plasma treatment to enhance the compatibility of cellulose fibers to the matrix [1]. For reference to plasma treatment we selected atomic layer deposition (ALD) which can be used for modification of surface properties of cellulosic fibers [8].

Plasma treatment is an extremely versatile technique for surface modification of various materials, such as rubbers, papers, fabrics, nonwovens, metals and especially polymer coatings. The advantage of this technique is that plasma treatment changes only the utmost atomic layers of material surface without modifying the bulk properties. Plasma contains activated species, including electrons, ions, excited radicals, atoms and UV-radiation, which are able to initiate chemical and physical modifications at the treated surface, and consequently improve e.g. wettability, adhesion, printability, biocompatibility, friction and heat resistance of surfaces [9][10]. The plasma-solid interactions at different surfaces can be classified to surface cleaning, etching or ablation, chemical modification and crosslinking [11]. It has been reported that plasma treatment improves the cellulose fiber-matrix adhesion by mechanical interlocking [12]. All interactions are contributing to plasma process at some degree, but the substrate, plasma gas, equipment design and operating parameters are defining which of the interactions is dominating the plasma process [9][10][11]. Low temperature plasma treatment is suitable even for heat-sensitive materials such as cellulose and polymer films. The effects of plasma treatment on the surface properties of polymeric surfaces have been quite extensively studied [11,13-19]. We have, for example, observed that plasma treatments can be used for surface treatment of cellulosic textiles: plasma activation or hydrophilization and plasma deposition (siloxane) for hydrophobization of textile surfaces [20]. However, not so many plasma studies exist on cellulose reinforcement materials and none for foam formed nonwoven reinforcements.

Atomic layer deposition (ALD) is a surface controlled layer-by-layer coating method. ALD is based on self-limiting gas-solid reactions leading to coatings with low impurity content. ALD allows the preparation of dense and pinhole-free inorganic films that are uniform in thickness even deep inside pores, trenches, and cavities of various dimensions, and is thus suitable coating method for porous materials and high aspect ratio structures. We have shown process penetrates nonwoven like structures and coatings can be formed also on fibers within the structure [21][22].ALD has become an important technique for depositing inorganic and hybrid thin films for a variety of materials for variety of applications. In our earlier work low temperature ALD process has been proven suitable for coating of various polymeric surfaces [23][24][25][26]. We have demonstrated that low-temperature atomic layer deposition (ALD) can also be used as a tool to adjust surface properties such as wetting characteristics of polymeric surfaces. Just a few ALD cycles of Ti_2O and Al_2O_3 affected the surface characteristics of the nonwoven material [8]. Therefore we assume that we can also affect fiber to matrix adhesion with ALD.

Foam is an advanced suspending medium that can be applied in several industrial-scale applications. Foams have been utilized conventionally in long-fibre based nonwoven industry [27]. Typical product applications are specialty papers, filter materials and different kind of technical textiles. In the paper industry, foam-laid forming technology has been demonstrated in the 1970 in a pilot scale based using the so called Radfoam process [28]. Radfoam process was found to enhance significant product properties and especially formation in nonwoven and paper applications [29]. The air content of foam forming process was typically in the range of 60 – 70%.

The object of our research was to improve cellulose fibres surface properties by air plasma and ALD treatment for a better adhesion between foam formed cellulose reinforcement sheets and epoxy resin.

2 MATERIALS AND METHODS

2.1 Materials

The present long-fibre foam forming studies were carried out both in laboratory and in the semi-pilot scale. The target was to produce either viscose fibre sheets or a viscose fibre based reel utilizing foam forming technology, which can be further used in converting studies. Kelheim viscose fibres of the length 6, 12 and 24 mm were used. The foam structure and rheology effectively prevents long-fibre entanglement and the build-up of unwanted yarns in the process. In particular, the flocculation tendency of the fibres is much smaller for the foam-laid process than for the water-laid process. We were able to make very homogeneous nonwoven up to 24 mm viscose fibres using a laboratory foam forming process (see Figure 1). The consistency used in this procedure was clearly higher than in typical water laying processes for nonwovens. The shear rate of the flow was tuned suitable when mixing the fibre suspension and the foam together [30]. The shear rate had to be high enough to break the fibre bundles, and at the same time not too high to cause intensive interactions between the fibres. The produced sheets from long-fibre foam forming studies were taken further to the converting trials.

Generally, foam forming process is suitable for producing a wide range of tailored nonwoven materials based on cellulose raw materials. Foam properties and pre-processing and forming procedures have a central role for the flocking tendency and the homogeneity of the final structure. With suitable foam structure and viscosity, fibre flocking leading to structural non-uniformity can be largely avoided.

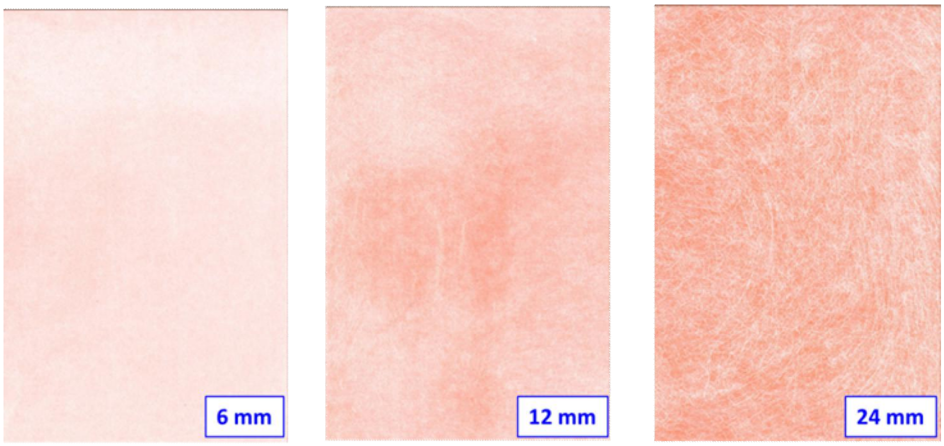

Figure 1: Foam-formed laboratory sheets obtained with viscose fibres. The homogeneity of the structure is preserved for the varied fibre lengths (6, 12 and 24 mm).

The laboratory sheets were made with 100% viscose fibers ordered from Kelheim, whose mass/length ratio was 1.7 dtex. The fibers were delivered in the form of aligned small bundles at 50% moisture content. The wet foams were produced with the ionic surfactant sodium dodecyl sulphate (SDS, Sigma-Aldrich) with 90% purity. After making the foam, latex (Celanese Co., Mowilith TE 157 S) was added in the wet fiber foam in order to increase the strength of the formed structure. Complete nonwoven foam formed sheets had weight 50+50 grams per square meter.

2.2 Plasma treatment

Atmospheric plasma treatment was used to modify foam formed nonwoven sheets at the pilot line of Tampere University of Technology (TUT)/Paper Converting and Packaging Technology (Figure 2). This unique pilot line has possibilities for (co)extrusion coating and lamination, cast film production and dispersion coating. Furthermore, several surface modification technologies are available including corona, flame and atmospheric plasma.

Figure 2: Extrusion coating and lamination pilot line at Tampere University of Technology. Maximum line speed at the pilot line is ~ 400 m/min and maximum web width 550 mm.

In this study we used plasma system PlasMatrix® from AFS, which can be used for surface activation and fine cleaning of various materials (Figure 3). PlasMatrix® is a multi-jet plasma system with controlled arc discharges in air. The plasma is produced by passing air through a high-voltage field, where it is blown out of the unit, producing a potential-free energy source which is used for surface modification [17]. It has been reported that increase of plasma treatments output from 0,5 kW to 1 kW do not have noticeable effect on the contact angle but increasing the number of cycles from 10 to 50 has pronounced effect on wettability [4].

Foam formed cellulose sheets, reference and sample, were divided to half (50 g/m^2) and paper taped from edges to board filmstrip. Reason for taping the reference sample was that equal amount of pressure compared to samples is also affecting the reference sample. For surface activation of foam formed cellulose fiber reinforcement, two different outputs were used 8 kW and 12 kW, while line speed was kept constant (100 m/min).

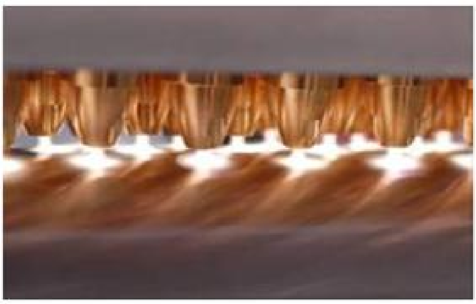

Figure 3: PlasMatrix® from AFS.

2.3 ALD treatment

In this study we used ALD produced thin films in order to increase hydrophobicity of cellulose fiber surface in order to improve fiber-matrix adhesion in composite structure. Foam formed samples (50+50 g/m^2) were ALD coated (SUNALE R200 ALD reactor, Picosun Oy) with ten cycles of Al_2O_3 or TiO_2 at 100°C. Reactants for TiO_2 and Al_2O_3 were $TiCl_4$ and water and trimethyl aluminium (TMA) and water, respectively.

2.4 Manufacture of composite structure

Composite structures with thermosetting matrix and natural based fibers are commonly manufactured using manufacturing methods such as wet lay-up, resin transfer molding, compression molding and vacuum assisted resin infusion [7]. I.W. Low *et al*. [31] noted that method of mixing the fibers with resins is usually based on mechanical blending or stirring. Drawbacks of these methods are not allowing incorporating large quantities of fibers that high fiber volume fraction can be achieved and has a tendency to cause fiber damage, agglomeration and generate unwanted air bubbles to the composite structure. In this study laminated composite structures were manufactured using vacuum assisted resin infusion to maximize fiber content, better mixing between the matrix and fibers and more precise fiber spacing with uniform thickness in final laminated cellulose-epoxy composite structure [4].

Six layers of ALD treated and respectively 12 layers of plasma treated foam formed cellulose sheets were stacked and introduced with resin via infusion (Figure 4). Used resin was Epikote MGS RIMR 135 epoxy resin with Epikure curing agent MGS RIMH 137, mixing ratio 100:30 by weight. This epoxy system is specially designed for infusion processes and used for example in sports equipment [32]. After infusion samples were post cured 24h @ RT and 6h @ 80 ^{o}C.

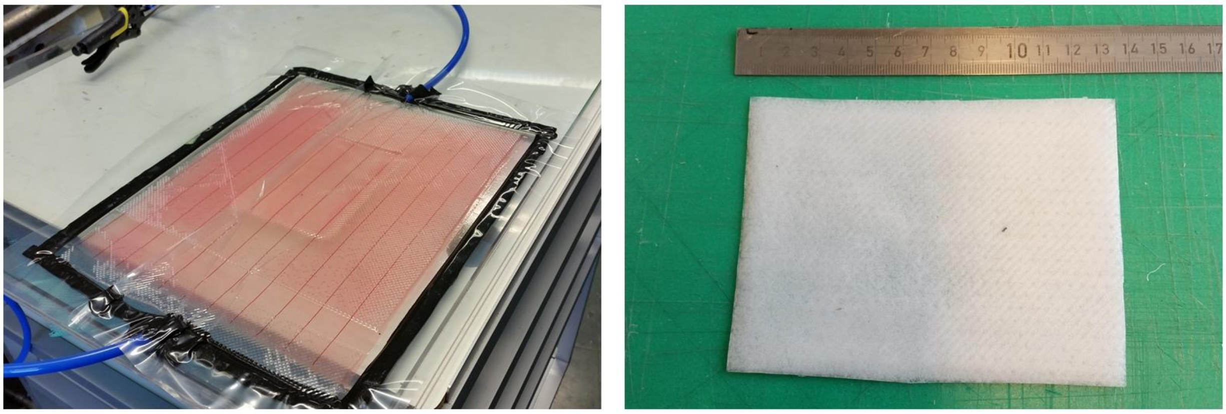

Figure 4: On the left vacuum assisted resin infusion of the sample. On the right is ready laminate sample 13 x 10 cm.

During the infusion process it was noted that the surfactants used in the foam forming process are present in fibres surfaces and caused large quantities of gas/air bubbles in the injected epoxy resin. To minimize the amount of bubbles in composite structure and voids in final composite structure, some epoxy resin was infused through injection area with the purpose to move bubbles from cellulose reinforcement to the resin trap.

2.5 Interlaminar shear test (ILSS)

The interlaminar shear strength (ILSS) was determined to estimate the interfacial adhesion strength of the composite structures. The ILSS tests were conducted according to ASTM D 2344 standard at crosshead speed of 1mm/min and span to thickness ratio of 4 (Figure 5).

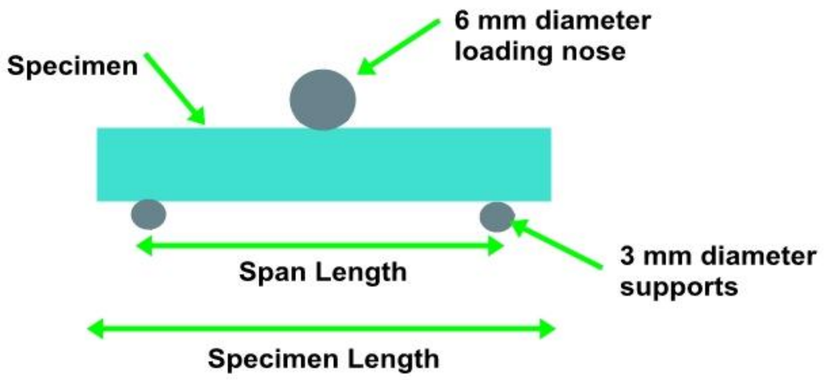

Figure 5: ILSS test configuration

The ILSS was calculated using equation 1:

$$ILSS = 0{,}75\frac{P_b}{b * d} \quad (1)$$

Where P_b is maximum load (N), b is the width of the specimen (mm) and d is the thickness of the specimen (mm). A minimum of 8 specimens per treatment were water jet cut and tested.

3 RESULTS

The ILSS values were used to determine whether the surface treatments improve the fiber-matrix adhesion in the studied cellulose epoxy composites. The ILSS results of all six composite laminates with standard deviation are shown in Figure 6.

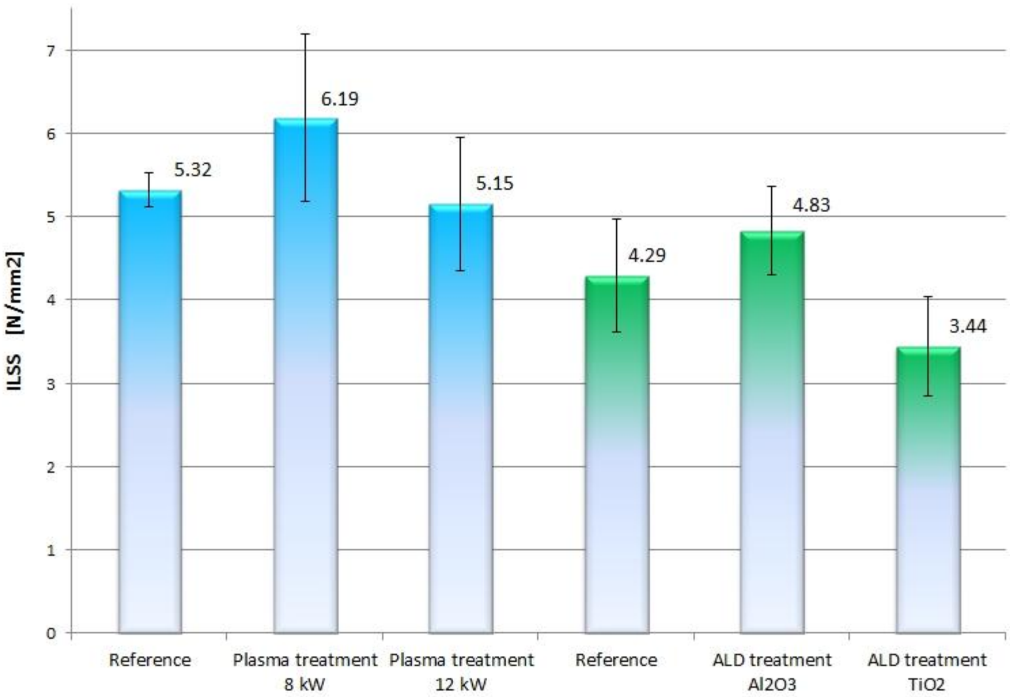

Figure 6: The ILSS results for the plasma and ALD treated samples and corresponding untreated reference samples.

In blue columns, the effect of plasma treatment can be seen. Due to relatively high standard deviation of the plasma treated composite results, it is not clear if the plasma treatments increased the adhesion between epoxy resin and cellulose fibers. In average, 8 kW plasma treatments had a positive effect on adhesion and increased the ILSS values but also large standard deviation has to be noted.

In green columns, the effect of ALD treatments can be seen. On average, a positive effect can be seen in Al_2O_3 treated samples but TiO_2 ALD treatment seems to have a negative effect on the ILSS values of the composite structure.

Comparison to epoxy manufactures glass fiber- epoxy and carbon fiber- epoxy structures ILSS values 42-55 N/mm^2 it is noted that our results are ten times smaller [28]. Reason for low ILSS values in our study can be explained with microscope pictures. In Figure 7 and 8 it can be seen that cellulose-epoxy structure contains large quantities of voids. These voids are formed in the infusion process when epoxy resin started to bubble. In all samples (ref, plasma and ALD) relatively large voids can be seen.

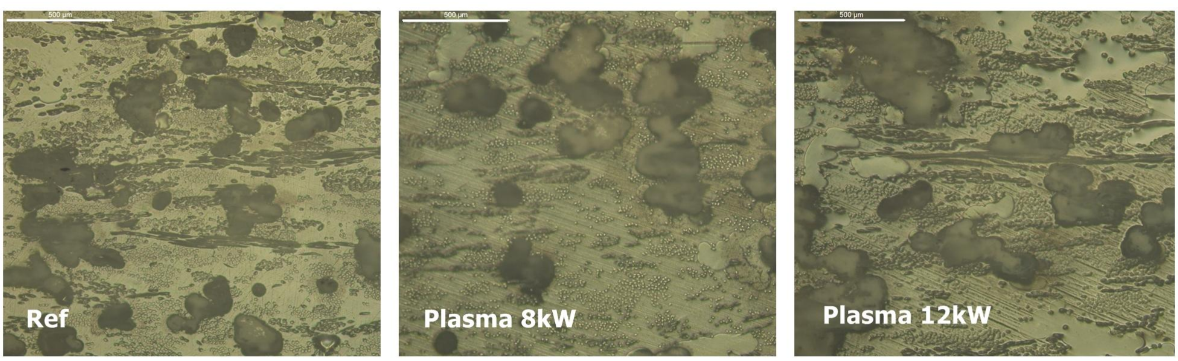

Figure 7: Microscope pictures of plasma treated samples and reference. Scale bar is 500 µm

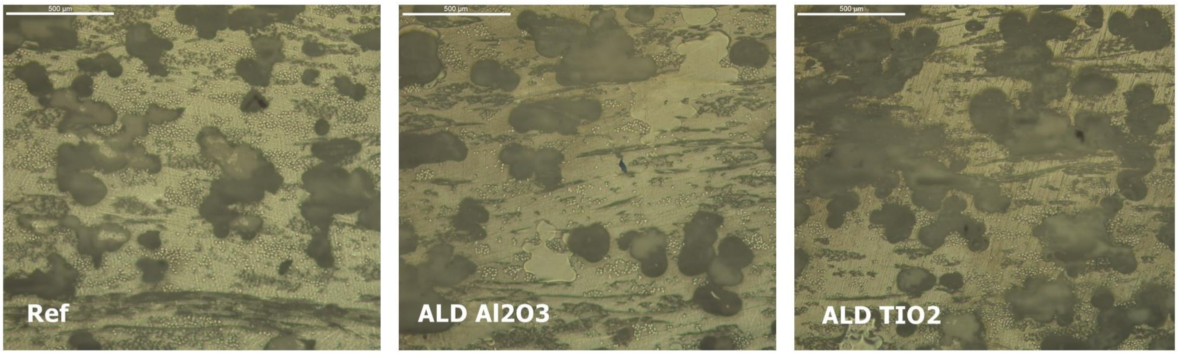

Figure 8: Microscope pictures of ALD treated samples and reference. Scale bar is 500 µm

4 CONCLUSIONS

The adhesion promotion treatments of nonwoven foam formed cellulose sheets have been carried out using plasma (8 kW and 12 kW) and ALD treatment with TiO_2 and Al_2O_3.

Surface treatment is crucial step when manufacturing composites reinforced with cellulose fibres, it is essential to reduce the hydrophilicity of fibres and therefore increase adhesion between matrix and gain better mechanical properties in the composite structure.

In our study, we used one cycle plasma treatment with the outputs of 8 kW and 12 kW. Plasma treatments effect on adhesion is debatable because of large quantities of voids in the composite structure. Same negative effect of voids can be seen in ALD treated samples.

Binder latex in foam formed nonwoven cellulose sheets can also affect the adhesion. One solution is to change the current binder to compatible binder material for example epoxy powder or unsaturated polyester powder.

ACKNOWLEDGEMENTS

The Finnish Funding Agency for Technology (Tekes) funded project Design Driven Value Chains in the World of Cellulose (DWoC) is acknowledged for financing this work. The authors also gratefully acknowledge Marikki Laamanen, Petri Kuusipalo, Anne Tauriainen, Meri Kiviniemi and Pasi Seppälä for their assistance in the experiments.

REFERENCES

[1] Ebru Bozaci, Kutlay Sever, Mehmet Sarikanat, Yoldas Seki, Asli Demir, Esen Ozdogan, Ismail Tavman, Effects of the atmospheric plasma treatments on surface and mechanical properties of flax fiber and adhesion between fiber–matrix for composite materials, Composites: Part B 45 (2013) 565-572

[2] Kutlay Severa, Mehmet Sarikanatb, Yoldaş Sekic, Gökhan Erkand, Ümit Halis Erdoğand, Seckin Erdenb, Surface treatments of jute fabric: The influence of surface characteristics on jute fabrics and mechanical properties of jute/polyester composites, Industrial Crops and Products 35 (2012) 22-30

[3] M. Ragoubi, B. George, S. Molina, D. Bienaimé, A. Merlin, J.-M. Hiver, A. Dahoun, Effect of corona discharge treatment on mechanical and thermal properties of composites based on miscanthus fibres and polylactic acid or polypropylene matrix, Composites: Part A 43 (2012) 675–685

[4] C.N. Flynn, C.P. Byrne, B.J. Meenan, Surface modification of cellulose via atmospheric pressure plasma processing in air and ammonia–nitrogen gas, Surface & Coatings Technology 233 (2013) 108–118

[5] Tingju Lu, Man Jiang, Zhongguo Jiang, David Hui, Zeyong Wang, Zuowan Zhou, Effect of surface modification of bamboo cellulose fibers on mechanical properties of cellulose/epoxy composites, Composites: Part B 51 (2013) 28–34

[6] N. Sgriccia, M.C. Hawley, M. Misra, Characterization of natural fiber surfaces and natural fiber composites, Composites: Part A 39 (2008) 1632–1637

[7] Abdullah A. Kafi, Kevin Magniez, Bronwyn L. Fox, A surface-property relationship of atmospheric plasma treated jute composites, Composites Science and Technology 71 (2011) 1692–1698

[8] M Vähä-Nissi, J Sievänen, E Salo, P Heikkilä, E Kenttä, LS Johansson, JT Koskinen, A Harlin, Atomic and molecular layer deposition for surface modification, Journal of Solid State Chemistry, 214, June 2014, 7–11

[9] C. M. Chan, T.M. Ko and H. Hiraoka. *Surface Sci. Reports*, 24, 1–54 (1996).

[10] M. Strobel, C. S. Lyons, K. L. Mittal. *Plasma Surface Modification of Polymers: Relevance to Adhesion*. VSP, Utrech, Netherlands (1994).

[11] S. L. Kaplan. *Surface and Coatings Technology*, Vol. 186, 214–217 (2004)

[12] E. Bozaci, K. Sever, A. Demir, Y. Seki, M. Sarikanat, E. Ozdogan, Effect of the atmospheric plasma treatment parameters on surface and mechanical properties of jute fabric, Fiber Polym, 10 (6) (2009), pp. 781–78

[13] N. De Greyter, R. Morent, C. Leys, L. Gengembre and E. Payen. *Surface Coatings Technol*. 201, 7066–7075 (2007)

[14] J. B. Lynch, P. D. Spence, D. E. Baker and A. Postlethwaite. *J. Appl. Polym. Sci.* 71, 319–331 (1999)

[15] M. C. Coen, G.Dietler, S. Kasas and P. Gröning. *Appl. Surface Sci*. 103, 27–34 (1996).
R. Mahlberg, H. E-M Niemi, F. S. Denes and R. M. Rowell. *Langmuir*. 15, 2985–2992 (1999).

[16] O-J. Kwon, S. Tang, S-W. Myung, N. Lu and H-S. Choi. *Surface Coatings Technol*. 192, 1–10 (2005)

[17] Tuominen, Mikko; Lahti, Johanna; Lavonen, Juho; Penttinen, Tapani; Räsänen, Jari P.; Kuusipalo, Jurkka 2010. The influence of flame, corona and atmospheric plasma treatments on surface properties and digital print quality of extrusion coated paper. Journal of Adhesion Science and Technology vol. 24, num. 3, 471-492.

[18] Tuominen, Mikko; Lavonen, J; Lahti, J; Kuusipalo, J. 2013. Atmospheric Plasma Treatment in Extrusion Coating: Part 2 Surface Modification of LDPE and PP Coated Papers In: Thomas, Michael; Mittal, K.L. (ed.) Atmospheric Pressure Plasma Treatment of Polymers, Relevance to Adhesion, Hoboken, New Jersey, John Wiley & Sons; Scrivener Publishing 355-381.

[19] J. Lahti, J. Lavonen, H. Christophliemk, 14th TAPPI European PLACE Conference 2013 Dresden.

[20] K. Nättinen, J. Nikkola, H. Minkkinen, P. Heikkilä, J. Lavonen, M. Tuominen, Reel-to-reel inline atmospheric plasma deposition of hydrophobic coatings , Journal of Coatings Technology and Research . Vol. 8 (2011) No: 2, 237-245, doi: 10.1007/s11998-010-9292-z

[21] P. Heikkilä, H. Hirvikorpi, H. Hildén, J. Sievänen, L. Hyvärinen, A. Harlin, M. Vähä-Nissi, High surface area nanostructured tubes prepared by dissolution of ALD-coated electrospun fibers, Journal of Materials Science . Vol. 47 (2012) No: 8, 3607-3612, doi: 10.1007/s10853-011-6207-z

[22] P. Heikkilä, A.T. Pasanen, M. Putkonen, M. Vähä-Nissi, Core-shell carbon-ceramic fibres by electrospinning and atomic layer deposition (ALD), E-MRS 2014 Fall Meeting, 15 - 18 September 2014, Warsaw, Poland (2014)

[23] J. Vartiainen Y. Shen, T. Kaljunen, T. Malm, M. Vähä-Nissi, M. Putkonen, A. Harlin,. Bio-based multilayer barrier films by extrusion, dispersion coating and atomic layer deposition. Journal of Applied Polymer Science (2015) - early access Wiley doi: 10.1002/app.42260

[24] T. Hirvikorpi, R. Laine, M. Vähä-Nissi, V. Kilpi, E. Salo, W.M. Lia, S. Lindfors, J. Vartiainen, E., Kenttä, J. Nikkola, A. Harlin, J. Kostamo, J. Barrier properties of plastic films coated with an Al_2O_3 layer by roll-to-toll atomic layer deposition , Thin Solid Films. Elsevier. 550 (2014) 164 – 169, doi: 10.1016/j.tsf.2013.10.148

[25] M. Vähä-Nissi, T. Hirvikorpi, J. Sievänen, K. Matilainen, E. Salo, A. Harlin, Atomic layer deposition of thin inorganic coatings onto renewable packaging materials, Solid State Phenomena, 185 (2012), 12-14, doi: 10.4028/www.scientific.net/SSP.185.12

[26] T. Hirvikorpi, M. Vähä-Nissi, J. Nikkola, A. Harlin, M. Karppinen, Thin Al_2O_3 barrier coatings onto temperature-sensitive packaging materials by atomic layer deposition, Surface and Coatings Technology. 205 (2011) 5088-5092, doi: 10.1016/j.surfcoat.2011.05.017

[27] Hanson James P., 1977

[28] B. Radvan, A. P. J. Gatward, the Formation of Wet-Laid Webs by a Foaming Process, Tappi 55 (1972) 748.

[29] M. K. Smith, V. W. Punton, A. G. Rixson, The structure and properties of paper formed by a foaming process, Tappi 57 (1974) 107-111.

[30] J. A. Ketoja, J. Lehmonen, A. Tanaka, Foam forming of long fibres, to be published.

[31] I.M. Low, M. McGrath, D. Lawrence, P. Schmidt, J. Lane, B.A. Latella, K.S. Sim, Mechanical and fracture properties of cellulose-fibre-reinforced epoxy laminates, Composites: Part A 38 (2007) 963–974

[32] Technical data sheet Hexion, Epikote Resin MGS RIMR 135