Extensible Cellulosic Fibre-polyurethane Composites Prepared *via* the Papermaking Pathway

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Formable papers can be used as an alternative to rigid plastics for making 3D shapes for packaging applications. However, commercial use of formable paper is currently limited, due to its poor extensibility. Cellulosic fibres can be combined with polyurethanes to improve the deformability of resulting fibre-polymer composites. This work describes the effect of spray and wet-end addition of polyurethane dispersions to paper to enhance the extensibility and formability of paper. The increase in extensibility was directly proportional to the amount of polyurethane retained in the paper. Absolute improvements in extensibility were as high as 4 to 6 percentage points. Improved extensibility resulted in better formability of paper, which eventually could allow it to compete with plastic packaging in certain applications.

Keywords: Extensibility; Deformation; Formability; Bonding; Packaging; Fibre; Polyurethane composite

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INTRODUCTION

Paper and paperboard packaging materials have proved their usability and importance over the last century. Deservedly, paper and paperboard are the most-utilized consumer and industrial packaging materials in the world (Smithers PIRA 2015). This is due to the advantageous features of paper, such as recyclability, renewability, special haptics, printability, and its excellent stiffness and strength per weight ratio in the dry state. However, paper and paperboard lack barrier properties against water vapour, oxygen, and grease permeation. Paper is also limited in terms of convertibility, *i.e.*, how many shapes of packages can reasonably be considered as designs in comparison to common plastics used in packaging. Overcoming these two principal issues would increase the competitiveness of paper in comparison to plastics. If the barrier properties of paper can be improved via the introduction of barrier films and coatings, which can also be made of renewable material and would not impair paper's recyclability (Vartiainen et al. 2014), this would eventually lead to an increased share of recyclable and renewable packaging on the market (Andersson 2008). Another drawback of paper is that its limited convertibility originates from its insufficient formability, which cannot be improved in the same way as the barrier performance. Due to this, paper and paperboard come in the form of rectangular boxes, tubes, and pouches, while complex 3D shapes cannot be formed from paper. The potential to utilize form-fill-seal type of packaging lines in producing modified atmospheric tray of blister type of packages for food and pharmacy products would be of great benefit.

Previously, the mechanical treatment of fibres, addition of natural polymers, increased drying shrinkage of paper, and compaction of the fibre web have been employed as strategies to improve the formability of paper (Zeng *et al.* 2013; Vishtal and Retulainen 2014a, 2014b; Vishtal *et al.* 2015). The addition of elastoplastomers, such as polyurethanes (PU) to the paper furnish or to the already formed paper web, is another method of modifying the deformation characteristics of paper towards the higher extensibility and formability required for 3D forming. Such attempts were made in the 1970s (Alince 1977, 1979); however, the results have not led to further applications in packaging. Paper-plastic composites can be manufactured *via* several approaches including the addition of polymer dispersions in the pulp slurry, impregnation of the formed paper web, or lamination of the dry paper web with plastic film.

Based on the work of Li and Ragauskas (2011), it can be deduced that the main challenges faced in the combining of cellulosic material and polymers, such as polyurethanes, are the even distribution of the polymer and maintaining the adhesion between cellulose and polymers while preserving the web-like structure of paper. PU is an interesting and versatile material due to its mechanical and chemical properties. It has a high elongation capability, in the range of 400 to 800% (Kojio *et al.* 2010). The properties can be controlled by the relative proportion of the constituent monomers, so that the product can be thermoplastic, compostable, applied as a waterborn adhesive, and presumably it has some compatibility with cellulose.

In this work, the effect of the addition of PU on the extensibility and formability of fibre networks was studied and evaluated using tailor-made testing equipment, conventional tests, and structural analysis performed using SEM and light microscopy. Two different commercial polyurethanes were used in this study, and they were introduced to paper either as a furnish additive to the pulp suspension or sprayed on the paper after wet pressing. These methods were deemed to be compatible with modern board machine environments. Composite structures with a polyurethane content from 10 wt% to 50 wt% were prepared.

EXPERIMENTAL

Materials

Pulp

The bleached, once-dried softwood kraft pulp that was used in this study was kindly provided by Stora Enso Oy and originated from their pulp mill in Imatra, Kaukopää, Finland.

Polyurethane dispersions

Based on preliminary tests, two different polyurethane dispersions were used in this study. The Impranil® DL519 was kindly supplied by Bayer AG (Leverkusen, Germany) as the 40 wt% dispersion (the average PU particle size was 110 nm), hereafter referred to in the text as PU "A". The Epotal® P 100 Eco was kindly supplied by BASF SE (Ludwigshafen, Germany) as a 40 wt% (particle size was below 100 nm), hereafter referred to in the text as PU "B".

Fixing polymer

The water solution of cationic coagulation and fixing polymer, Fennofix® 50 (Polydiallydimethylammoniumchloride), was kindly supplied by Kemira Oyj (Helsinki, Finland) as 40 wt%.

Methods

Mechanical treatment of fibres

The pulp was subjected to the sequential high- (Wing refiner) and low-consistency (Valley beater) mechanical treatments to improve the extensibility of the fibres and paper made of such pulp. High-consistency treatment creates micro-compressions and dislocations in the fibres, while low-consistency refining straightens the fibres and improves bonding (Zeng *et al.* 2013). The detailed effects of combined high- and low-consistency treatments on fibre and paper properties can be found in Khakalo *et al.* (2017).

Handsheet preparation

Handsheets were prepared according to ISO 5269-1 (2005) with a target grammage of 60 g/m². The handsheets were dried with and without drying restraint. Due to drying shrinkage and the addition of PU, the basis weights of the handsheets were in the range of 61 g/m² to 113 g/m². High basis weight (300 g/m²), A4-sized sheets for 3D forming were prepared using the "Juupeli" sheet former developed by VTT Technical Research Centre of Finland (Jyväskylä, Finland) and used in several studies (*inter alia* Oksanen *et al.* 2011). The types of the handsheets prepared in this study, their grammages, and densities are summarized in Table 1.

Sample	BW (g/m ²)	BW (g/m ²)	Density (kg/m ³)	Density (kg/m ³)
	A	В	A	В
Wet-end Addition				
REF	69.8 (65.2 rstr)	N/A	509 (631 rstr)	N/A
10%-PU	68.7 (61.3)	N/A	498 (619)	N/A
20%-PU	73.1 (65.8)	N/A	518 (633)	N/A
30%-PU	75.4 (68.5)	N/A	489 (591)	N/A
40%-PU	85.1 (76.8)	N/A	502 (586)	N/A
50%-PU	93.1 (83.7)	N/A	505 (585)	N/A
Spray Addition				
10%-PU	75.1	75.5	536	539
20%-PU	83.2	82.5	564	553
30%-PU	92.4	89.8	607	579
40%-PU	102.8	97.4	648	605
50%-PU	111.3	107.5	666	651
50%-DS*	112.1	109.6	690	645
HBW 30%-PU**	289.2	N/A	513	N/A

Table 1. Handsheet Type, Grammage, and Density: "A"- Bayer Impranil DL 519and "B"- BASF Epotal P100

Note: rstr - restrained dried, N/A not available, BW- basis weight, DS*- two-side addition, **- high basis weight (HBW)

Wet-end addition of polyurethanes

Due to electrostatic repulsion between pulp fibres and PU particles (both anionic), in the absence of some kind of fixative or retention aid, the PU is not well retained in the paper sheet during drainage. Therefore, to retain PU on fibres, a cationic high-charge density, low molecular weight polymer was added to the pulp-PU suspension. The schematic representation of this approach is shown in Fig. 1.



Fig. 1. Schematic representation of the method for addition and retention of polyurethane particles in paper furnish

Pulp fibres were diluted to form an approximately 2.5% consistency suspension having a volume of 1 L after this PU dispersion was added. This suspension was mixed for 10000 revolutions in a British pulp disintegrator, and a sample of filtrate was taken for turbidity analysis (see below). Subsequently, a fixing polymer was added in a proportion of 500 g per 100 kg of PU (0.05 g per 1 g of PU). After this, mixing continued for another 30000 rpm and another sample was taken for turbidity analysis. Additionally, a benchmark sample was prepared to evaluate the retention of PU in the handsheet mould (*i.e.*, dilution to 9.5 L), where the amount of retained PU was gravimetrically measured.

Evaluation of retention of PU in paper

The weight increment of the handsheets prepared from pulp-PU dispersion, in comparison with reference handsheets, was used for gravimetric retention evaluation. The value was derived from averaging the 10 handsheet measurements.

Turbidity measurement

Turbidity was measured for the undiluted filtrates, which were filtered through fine screen (300 mesh) to separate the pulp fibres. Turbidity was measured before and after the addition of the fixing polymer. The HACH 2100N (HACH company, Loveland, CO, USA) turbidity meter was used for the measurements.

Spray addition of polyurethanes

The PU was added to the wet fibre network after wet pressing by spraying. For the low-grammage handsheets, undiluted PU suspension (40 wt%) was added from top side, or in one case (50% addition) from both sides. A universal electrospray gun (Wagner W 140P, J. Wagner GMBH, Germany) was used. To enhance the penetration of PU into the paper, it was placed on a vacuum suction box.

The amount of the sprayed PU dispersion was gravimetrically controlled by weighing wet paper samples after spraying. Preparation of the restrained dried handsheets was not possible due to the high adhesion of PU to the drying plate.

Light microscopy

The images were taken using the Nikon Microphot microscope (Nikon Corporation, Tokyo, Japan) equipped with a CCD (Charge-Coupled Device) camera. The light strength was adjusted in the range of 4.3 to 10.7 in accordance with the magnification used. In each case, the exposure time was set as 10 ms.

Scanning electronic microscopy

Imaging was carried out with a Zeiss Sigma VP (Carl Zeiss NTS Ltd., Oberkochen, Germany) field emission scanning electron microscope (SEM) using an acceleration voltage of 3 kV to 4 kV. Prior to the imaging, the samples were attached to aluminium SEM stubs with carbon tape followed by sputter-coating (Emitech K100X, Emitech SAS, Paris, France) with platinum, forming a thin layer of 10 nm to 15 nm to avoid charging. The cross-sectional images of sheets were taken after resin embedding.

Dynamic mechanical analysis (DMA)

A dynamic mechanical thermal analysis was conducted for the polyurethanes used. Film samples made of the PUs were tested in shear mode using the Mettler Toledo DMA/STDA 861e instrument (Greifensee, Switzerland). The testing frequency was 1 Hz, and temperature range was -50 °C to 120 °C. Some sheet samples were tested in tensile mode under the same conditions.

Formation (grammage uniformity)

Formation was measured using beta radiation and a storage phosphor screen as done by Lappalainen *et al.* (2010).

Stress-strain measurements, formability strain, and 3D forming of paper

Tensile strength and strain at break of the paper samples were determined in accordance with the ISO 1924-2 (2008) standard. The 'formability strain' term refers to the highest strain that the paper experiences during the forming process in the 2D formability tester (VTT Technical Research Centre of Finland, Jyväskylä, Finland) before it breaks.

The formability strain is calculated from the position of the pressing die. Details of this measurement can be found in Vishtal and Retulainen (2014a). The 3D shapes were prepared using the 3D forming device at VTT. The device utilizes the hemispherical non-heated forming die (65-mm diameter) and the respectively shaped female forming cavity. The diameter of the samples was adjusted to 130 mm. Blank holding force of 2.5 kN was applied on the rim area of the sample (~100 cm²). The resulting pressure prevented any sliding and wrinkle formation under the circular blank holder.

RESULTS AND DISCUSSION

The beneficial effect of PU addition on formability depends on the evenness of its distribution in the paper and on the formation of adhesive PU-PU and PU-fibre-PU bonding. Two different addition methods were applied in this study: wet-end addition and spraying.

Wet-end Addition of PU

The addition of synthetic polymers to paper furnish is a known method for improving the dry strength of paper (Mihara and Yamauchi 2008); however, this technique had not been used before with polyurethanes. Polyurethane particles are negatively charged, as are cellulosic fibres, causing electrostatic repulsion and impairing the retention of PU. By adding a highly charged, low molecular weight cationic polymer in the thick stock, this adverse effect can be mitigated by "fixing" polyurethane particles on the surface of fibres. This approach is similar to that used for mineral fillers (Cadotte *et al.* 2007).

Without the addition of the cationic fixing agent, the retention of PU in the paper furnish was almost non-existent. However, at the same time, a high amount of fixing agent additions did not necessarily improve the ultimate retention of PU. A certain optimal addition level did exist. It was found that at the addition level of the cationic fixing agent of 1 kg per 100 kg of PU added to 1 ton of pulp, the clarity of the filtrates considerably increased, which indicated improved retention of PU on the fibres (Fig. 2).





The increase in clarity of the filtrates was likely to be associated with the electrostatic attachment of the PU particles to the pulp fibres; this was visually confirmed by the light microscopy images shown in Fig. 3.

As shown in Fig. 3, polyurethane particles were attached to the fibres irrespective of the amount of PU added. The PU particles tended to attach to fines, at places where the fibre was fibrillated, or where the cell wall structure was somewhat damaged. This could be explained by the higher surface area and higher density of accessible carboxylate groups in these areas of fibre and consequent higher attraction to the positively charged coagulant. The increase in the PU load on fibres led to an extensive agglomeration of PU particles, and at a PU load of 50% the agglomeration mechanism dominated and the attachment of PU to fibres was almost absent. In this case, the mechanism of retention was likely to be

filtration based. It was concluded that the addition of more than 30% PU on fibres may not have been feasible due to the unevenness of distribution and unevenness in mechanical properties, as well as the negative effect on recyclability of such structures.



Fig. 3. The agglomeration of fibres, fines, and PU particles after addition of the fixing agent at different magnifications: A) 100 kg PU/t of pulp and 1 kg/t of pulp fixing agent; B) 300 kg PU/t of pulp and 3 kg/t of pulp fixing agent; and C) 500 kg PU/t of pulp and 5 kg/t of pulp fixing agent



Fig. 4a. The influence of the PU "B" on the stress-strain properties and drying shrinkage of unrestrained dried paper-PU composite material, when PU was added to the pulp slurry. The REF refers to unrestrained dried paper without any additives and the error bars represent 95% confidence limits

The effect of wet-end addition of PU on the strength and extensibility of paper

The main purpose of the PU addition was to improve the formability of paper *via* improving its deformation characteristics, mainly extensibility. The influence of the wetend addition of the PU "B" in amounts of 10%, 20%, 30%, 40%, and 50% on the strain at break, tensile strength, and drying shrinkage of the unrestrained dried paper is shown in Figs. 4a and 4b.



Fig. 4b. The influence of the PU "B" on the stress-strain properties and drying shrinkage of restrained dried paper-PU composite material, when PU was added to the pulp slurry. The REF refers to unrestrained dried paper without any additives and the error bars represent 95% confidence limits

The addition of 20 wt% PU to paper furnish increased the strain at break from 11% to 13.5% in unrestrained-dried sheets and from 5.8% to 6.7% in restrained-dried sheets, while at the same time tensile strength decreased. A minor increase in the drying shrinkage with the increase of PU loading could be explained by the contribution of the PU network shrinkage to the overall drying shrinkage of the structure. This, however, was accompanied by a decrease in tensile strength of the paper, which was probably due to weaker fibre bonding and worsened formation. Similar trends in the influence of PU on the strain at break and tensile strength were observed in the case of restrained-dried paper, with the exception of lower absolute values of strain at break and higher values of tensile strength (Fig. 4b). This suggested that there was no particular difference in the formation of PU-fibre-PU bonds in both of the cases considered.

Spray Addition of PU

In contrast to wet-end addition, the spraying of polyurethane dispersion did not require any use of retention chemicals. The retention of the PU particles in the wet papersheet simply followed mechanical entrapment and mutual adhesion mechanisms. Addition of the PU to an already formed fibre network probably affected inter-fibre hydrogen bonding to a lesser extent than a wet-end addition. The PU likely filled the voids and provided additional bonding between fibres that were previously non-bonded or where the bond area was relatively low. However, penetration and even distribution of the polymer particles in the z-direction of the paper was difficult to achieve because PU particles tend to agglomerate and clog the voids in the paper. The influence of the spray addition of the PU "A" and "B" on the extensibility, tensile strength, and drying shrinkage of the unrestrained dried paper is shown in Figs. 5a and 5b.

Spray addition of PU "A" improved the extensibility of paper by 2.5 to 3 percent points, which was only a moderate increase. At the same time, tensile strength decreased approximately 20% irrespectively of the amount of PU added. The drying shrinkage was not affected. The PU "B" demonstrated slightly different behaviour with respect to the modification of stress-strain properties of paper and drying shrinkage (Fig. 5b). In this case, the improvement in extensibility was gradual with the increase in PU dosage and reached an absolute increase of approximately 4%-points in the case of 50% PU addition. In contrast, with PU "A", addition of PU "B" increased the drying shrinkage of paper. The tensile strength decreased to a greater extent with PU "B" than in the case of "A", which indicated that it modified the fibre-fibre contacts. In both cases, the addition of PU over 30% to fibres did not seem to be feasible due to the decrease in tensile strength.

Despite being quite different in its average particle size, degree of polymerization and, presumably, chemical composition, the two polyurethane dispersions showed similar effects on the stress-strain properties of paper with a moderate increase in extensibility and respective decrease in tensile strength. These trends were more profound with increasing dosages of polyurethanes. This suggested that these polyurethanes, when sprayed, were acting according to the same mechanisms.



Fig. 5a. The influence of PU "A" addition on the stress-strain properties and drying shrinkage of unrestrained-dried paper-PU composite material. The PU was added to paper by spraying after wet pressing of handsheets; *PU was added from both sides, equally in a total amount of 50%.



Fig. 5b. The influence of PU "B" addition on the stress-strain properties and drying shrinkage of unrestrained-dried paper-PU composite material. The PU was added to paper by spraying after wet pressing of handsheets; *PU was added from both sides, equally in a total amount of 50%

SEM Analysis of the PU-fibre Structures

The SEM images (Fig. 6) revealed that at 10% wet-end addition, the PU was evenly distributed on the papersheet in-between the fibres with no major agglomerations of the PU. In contrast, at an addition of over 30%, the PU started to agglomerate. The distribution of the polyurethane in the z-direction can be seen in the cross-section image, where the paper-PU composite with 30% PU content is shown. It seemed that the PU was distributed evenly without any major agglomerations, which correlated with the attachment of particles shown in the light microscopy images (Fig. 3).

The overall appearance of the surface of paper-PU composites where PU was added by spraying (Fig. 7) was different from the wet-end addition of PU. At 10% of addition, no PU layer on the surface could be observed with minor bridging bonding between fibres due to penetration of PU into the wet fibre web. However, the overall picture at 30% of addition was different; a layer of PU on the surface of the paper was clearly distinguishable, but with disruptions in the PU layer that were likely to be caused by trapped air.

In spraying the penetration of PU into paper was limited which can be seen from Fig. 7. The paper had a very dense PU layer on the top surface with quite a few voids, which explained the almost unchanged density of the composites. The PU "A" showed somewhat different behaviour from PU "B" in respect to the penetration into the paper, at 10% it already formed an almost complete layer on the surface of the paper. This meant that practically no penetration took place. At 30% the paper surface was completely covered with PU.



Fig. 6. The surface structure of paper-PU composites containing (A) 10% PU "B", (B) 50% PU "B", and (C) a cross-sectional image of the paper-PU composite containing 30% PU "B" that was added to the wet-end



Fig. 7. The surface SEM images of the paper containing (A) 10% or (B) 30% of PU "B" added by spraying; and the surface SEM images of the paper containing (C) 10% or (D) 30% of PU "A" added by spraying

It could be concluded that the retention with wet-end addition of PU was difficult, but it was the more efficient method in terms of evenness of distribution of PU in the fibre web. Spray addition gave good retention, but, when sprayed only from one side of the paper, it caused two-sidedness because the PU dispersion was unable to penetrate through the paper. In both cases, wet-end and spray additions did not seem to provide any visually observable benefits at dosages above 30%. Furthermore, when the SEM images and mechanical performance of paper were compared, the optimal dosage seemed to be somewhere between 20% and 30%.

2D Formability of Paper-PU Structures

Despite quite minor absolute increases in the strain at break of the samples (Figs. 4 and 5), the influence of PU addition on the formability strain was higher (Fig. 8).

Figure 8 shows that the formability strain of the untreated paper at 80 °C (11.1%) was almost equal to the corresponding strain at break value (10.8%), while the paper containing PU added in the wet end exhibited an increase in formability in comparison with the strain at break values. This was likely induced by the thermal softening of polyurethane and the fibre-PU-fibre adhesive bonds. Some of the bond may be created not earlier than at the 2D forming stage. For the wet-end addition, the highest formability (16%) was exhibited by the sample containing 40% PU. An increase of PU content to 50% negatively affected formability, which was likely due to the remarkably impaired uniformity of paper.

Spray addition of PU also had a higher positive effect on the formability strain than the strain at break. The formability strain for both of the PUs at 30% addition was improved by 5%-points, with PU "B" performing a bit better at low addition levels. This indicated that the PU matrix between fibres had a better ability to distribute stresses when heated and softened. As shown, formability strain (Fig. 8) did not necessarily correlate linearly with the strain at break values (Figs. 4 and 5), which could be explained by the thermal softening behaviour of the composite structure.



Fig. 8. The influence of the PU addition on the formability strain (measured at 80 °C) of unrestrained-dried paper-PU composites

Dynamic mechanical analysis

A stronger softening behaviour of PU "B" in formability testing was also confirmed by dynamic mechanical analysis (Fig. 9). The thermal softening behaviour of PU "A" was much different from "B", the latter having a clear softening point around at 60 °C, while the former had a wider softening region between 65 °C and 80 °C (concluded from the storage and loss coefficient).

The storage modulus of PU "B" at 80 °C was also clearly lower than that of PU "A". The paper samples sprayed with the PUs did not show any change in their softening behaviour when tested in tensile mode, which suggested that the fibre properties dominated the resulting properties of composites.

Preparation of 3D shapes from paper-polyurethane composites

Paper samples treated with polyurethane were formed using the 3D forming device of VTT Jyväskylä, which was equipped with a hemispherical forming die. The blank holding force was adjusted in such a way as to avoid any sliding of the sample into the forming cavity and avoid the formation of wrinkles on the side rims. Thus, the 3D shape was formed almost entirely due to the multidimensional straining of the paper. The images of the formed 3D shape prepared from the paper sprayed with 30% PU "A" are shown in Fig. 10.

At room temperature the adhesion of fibres with PU "A" was earlier found to be better than with PU "B" (Kouko *et al.* 2018) but the better softening of PU "B" seemed to compensate for the difference in adhesion.



Fig. 9. Storage and loss moduli of PU "A" and "B" films from dynamical mechanical analysis

The maximum depth of the shapes produced from the paper treated with the PU was approximately 21 mm, which corresponded well to the previously obtained formability strain values. The successful forming of such shapes suggested that the deformability characteristics of paper were remarkably improved.



Fig. 10. Examples of the 3D shapes prepared with the 3D forming device at VTT, Jyväskylä; the depth of the shapes at the point of maximum curvature is approximately 21 mm (at diameter of the die of 65 mm)

CONCLUSIONS

- 1. The PU dispersions were added to paper by spraying and as a wet-end addition. The PU particles were effectively retained on fibres in water suspension according to the electrostatic mechanism using a so-called "fixing" approach by applying a highly charged cationic polymer.
- 2. In the suspension, PU particles were attached to fines or to places of extensive fibrillation in fibres. This was explained by the higher surface areas, increased density of accessible hydroxyl groups in these areas, and consequently a higher attraction to positively charged coagulant.
- 3. The addition of 20% to 30% of PU to paper improved the extensibility of paper by 3 to 4 percent points, while somewhat decreasing the tensile strength. Higher dosages of PU were not feasible due to the poor formation (wet-end addition) and notable two-sidedness of paper (spray addition).
- 4. The observed improvements in extensibility and formability were likely due to the increased bonding in paper on account of PU-PU and PU-fibre-PU bonds, increased drying shrinkage, and increased plastic deformation of the composite due to thermally induced softening of polyurethane.
- 5. Despite the visually different extent of penetration into the paper for the two polyurethanes used in this study, their influence on the formability of paper was quite similar, which suggests that chemical interactions between PU and fibres are quite weak.

ACKNOWLEDGMENTS

This work was a part of the ACel programme of the Finnish Bioeconomy Cluster FIBIC. The funding from the Finnish Funding Agency for Technology and Innovation (TEKES), and Academy of Finland is acknowledged. Mr. Henrik Lund (Bayer, now Covestro) and Dr. Anton Essner (BASF) are acknowledged for providing the PU dispersions for testing. Dr. Jonni Ahlgren (Kemira Oyj) is thanked for the valuable advice in the development of the fixing approach for PU retention and providing the highly charged cationic polymer. Ms. Mirja Nygård and Ms. Merja Selenius (VTT) are thanked for carrying out the DMA tests and for taking the light microscope pictures, respectively. Ms. Mari Hiltunen (Enso Oyj) is acknowledged for providing the SEM pictures.

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Article submitted: December 12, 2017; Peer review completed: April 22, 2018; Revised version received and accepted: May 14, 2018; Published: May 23, 2018. DOI: 10.15376/biores.13.3.5360-5376