An effect of carboxymethyl starch addition on adhesion to paper of water-soluble pressure-sensitive adhesive

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Research Article

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Abstract

Introducing biopolymer derivative, i.e. carboxymethyl starch into pressure-sensitive adhesives for paper industry has been proposed. Obtained adhesives were transferred onto water-dispersible paper carrier giving repulpable double-sided splicing tape. The effect of carboxymethyl starch degree of substitution on essential adhesive properties: tack, peel adhesion, as well as shear strength for steel and various papers has been tested. Additionally, the solubility in water and alkaline medium has been evaluated. The highest tack and peel adhesion increase was reported for PSA containing CMS with degree of substitution DS 0.86, to fax paper. Moreover, the dynamic shear strength test imitating the shear conditions in paper processing revealed, that the highest values of this parameters exhibited the system with 15 wt.% CMS DS 0.86. For this system the shortest water-dissolving times as well as at elevated pH were noted: 314 s and 60 s, respectively.

1. Introduction

Using water-soluble pressure-sensitive adhesive (PSA) is strongly recommended in paper processing industry. By transferring it on the water-repulpable substrate (e.g. paper tissue) - the water-dispersible splicing tapes could be obtained. Such tapes could be in a form of one-sided, double-sided or carrier-free (transfer) tapes. They are used for splicing the paper rolls' ends, and the same guarantee the process continuity. The splice must hold securely the two substrates (paper rolls) and prevent them from even slight separation, as it could lead to the undesirable adhesive layer exposure, and in consequence sticking surface and paper folding. The strong connection is required only during the paper passage through the production line. After that the splice is removed and recirculated.

Recently, applying water-soluble PSA for the self-adhesive labels has been reported (Antosik et al. 2015). The self-adhesive labels are commonly used in the packaging industry. Using water-soluble adhesives facilitates the separation of the label from the packaging during cleaning process. However, the labels should remain on packaging when exposed to the humidity or temperature changes during storage.

Although starch is one of the oldest binders used by human, very few reports on using polysaccharides in pressure-sensitive adhesive systems has been reported. However, bearing in mind the environmental concerns, introducing natural polymer into PSA should be considered. Application of acrylic-modified polysaccharides (mostly starch) was developed for fabric (Li et al. 2020) and wood adhesive purposes (Zia-ud-Din et al. 1018). In case of pressure-sensitive adhesives addition of starch nanoparticles covered with acrylates (Zhang et al. 2018 and 2020) or using modified starch nanocrystals for emulsion stabilization of acrylic PSA (acting also as a tackifying agent) (Ayed et al. 2020) was recently proposed.

In this paper repulpable pressure-sensitive adhesive tapes for paper processing industry were developed. The tapes consist of two main components: adhesive and carrier. The former was water soluble acrylic PSA containing carboxymethyl starch (CMS) with various degree of substitution (DS). As carrier the water-dispersible filter paper was used. Carboxymethyl starch is a derivative prepared in Williamson

reaction between starch and monochloroacetic acid or its sodium salt. Unlike native starch, it is soluble in cold water. Its physicochemical properties, i.e. solubility rate, depends on the average number of OH groups in a starch recurrent unit substituted with carboxymethyl groups, i.e. its degree of substitution (DS). An excellent film forming ability of high substituted CMS has been described (Wilpiszewska et al. 2015).

Introducing CMS into PSA system based on poly(acrylic acid) has been already reported (Wilpiszewska and Czech 2018). In this paper carboxymethyl starch with various DS (low, medium and high: 0.15, 0.6, and 0.86, respectively), was introduced into water-soluble PSA based on acrylic copolymer (comonomers: 2-ethylhexyl acrylate, butyl acrylate and acrylic acid). Subsequently, the double-sided adhesive tapes on dispersible in water filter paper carrier were prepared. The influence of CMS type on essential adhesive properties, i.e.: tack, peel adhesion and shear strength for various paper types (fax, newsprint, photographic and art paper) has been presented. Additionally, the dynamic shear strength has been determined. Moreover, solubility in water as well as in alkaline solution of prepared adhesives containing CMS has been tested.

2. Materials And Methods

2.1. Materials

Carboxymethyl starch with low degree of substitution (DS 0.15) was purchased from (Zetpezet, Poland). CMS with medium and high DS were prepared using potato starch from form Nowamyl S.A., Poland, and sodium chloroacetate, isopropanol, sodium hydroxide (microgranules) purchased from Chempur, Poland. For determination of CMS degree of substitution copper sulfate pentahydrate (Chempur), murexide and ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA) of Sigma-Aldrich (Germany) were used.

The industrially grade acrylate monomers: acrylic acid, butyl acrylate, 2-ethylhexyl acrylate as well as initiator AIBN were purchased from BASF. Technically grade: aluminum acetyl acetonate – AlACA (crosslinking agent) was from Wacker Chemie, propanol-2 was from Brenntag, water-soluble plasticizer polyethylene glycol-PEG 400 was from Evonik, and water-soluble dye Luconyl Green LG 9360 was from BASF. As the carrier the 12 g/m² coat weight water-dispersible nonwoven tea filter paper from Crompton was used.

2.2. Methods

2.2.1. Synthesis of medium and high substituted CMS and their characterization

Modification of potato starch was carried out in a batch reactor equipped with a mechanical stirrer, a thermocouple, and a capillary tube supplying nitrogen to the reaction system. Starch (13.6–14 wt.% moisture) was etherified in isopropanol/water in a one-step process. In the batch reactor, MCA was dissolved in isopropanol, and then water solution of NaOH was added. When the mixture became white and homogeneous, starch and remaining NaOH were introduced. Obtained product was filtered,

neutralized with glacial acetic acid, washed five times in 80 wt.% methanol aqueous solution, then washed once again in methanol and dried in the air.

Degree of substitution was measured according to method described by Kessel (1985). The CMS sample was moisturized by 1 mL of ethanol and dissolved in 50 mL of distilled water. Subsequently, buffer was added (NH_4Cl aqueous solution, 20 mL), neutral pH was adjusted, and then the whole mixture was poured into a measuring flask (250 mL) with 50 mL of $CuSO_4$ solution. After 15 min, the measuring flask was filled up with water and the whole content was filtered. Filtrate was titrated with EDTA solution using murexide as an indicator.

FTIR analyses of the prepared CMS were performed using Nexus FTIR Spectrometer Thermo Nicolet with Golden Gate ATR attachment. The resulting spectra were converted using the software OMNIC.

2.2.2. Synthesis of water-soluble acrylic PSA and its characterization

Into 1-liter reactor equipped with thermometer, mechanical stirrer, water cooler and dropping funnel the polymerization medium (solvent mixture 60 wt.% ethyl acetate and 40 wt.% acetone) was placed. The monomers mixture (35 wt.% 2-ethylhyxyl acrylate, 30 wt.% butyl acrylate and 35 wt. % acrylic acid) with 0.1 wt.% AIBN was dropped for 3 h into the boiled polymerization medium. The post-reaction time for reduction of free residue monomers was 4 h, and the polymer content after polymerization process was 40 wt.%.

The viscosity of the synthesized solvent-based acrylic pressure-sensitive adhesives was determined using Rheomat RM189 from Rheomatric Scientific, with spindle no. 3 at room temperature. The molecular weight studies were performed with a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck Hitachi, equipped with a PL gel 106 Å column from Hewlet Pacard.

2.2.3. Preparing water-soluble PSA containing CMS with various DS

The copolymer prepared from three monomers (ethylhexyl acrylate, butyl acrylate, and acrylic acid) was stabilized with 10 wt.% propanol-2, and subsequently modified with 0.4 wt.% AlACA according to polymer content, subsequently the plasticizer 50 wt.% PEG 400, 3 wt.% NaOH and green dye 0.1 wt.% Luconyl Green LG 9360 were added. To such a water-soluble acrylic PSA in the next step CMS 1, 3, 5, 7, 10 and 15 wt.% on a basis of copolymer content was added. The systems were stable for at least 3 week storage.

2.2.4. Preparing double-sided tapes with acrylic PSA containing CMS

Green water-soluble acrylic PSA modified with carboxymethyl starches with various carboxymethyl groups content was coated (60 g/m² coat weight), dried for 10 min at 110°C in drying canal and double-side transferred on a carrier – 12 g/m² coat weight water-dispersible paper (Fig. 1).

The resulted double-sided splicing tapes were tested for tack and peel adhesion on steel, as well as various paper types. Moreover, shear strength at 20°C and 70°C, dynamic shear strength, as well as bleeding tendency of splicing tapes were determined.

2.2.5. Characterization of double-side splicing tapes

The resulted adhesives were investigated for typical PSA properties, such as tack, peel adhesion and shear strength by standard AFERA (Assotiation des Fabricants Europeans de Rubans Auto-Adhesifs) procedures: AFERA 4015 (tack), AFERA 4001 (peel adhesion), AFERA 4012 (shear strength), and shear strength known as SAFT test.

The tack method according to AFERA 4015 is relatively simple and may be conducted using common tensile strength test machines. Loop-tack method measures the instantaneous adhesion of a loop of adhesive-coated material using no external pressure to secure contact, in other words it is the force required to separate - at a specific rate - a sticky material loop from a standard surface (Fig. 2).

A sample of acrylic/CMS PSA-coated material 1 inch (ca. 2.5 cm) wide and about 7 inch (ca. 17.5 cm) long was bonded to a horizontal clean steel test plate at least 10 lineal cm in firm contact. The steel test plate was clamped in the jaws of a Zwick tensile testing machine. The tape was peeled from the steel surface with a constant rate of 100 mm per minute, and the force in Newtons was recorded. In the paper industry the loop-tack method allows to measure tack using wide range of paper substrates.

The peel adhesion is the force required to remove a coated flexible pressure-sensitive adhesive sheet material from a test panel measured at a specific angle and removal rate. For 180° peel measurements (AFERA 4001) the results depend on the face stock material. A sample of acrylic/CMS PSA-coated material 1inch (ca. 2.5 cm) wide and about 5 inch (ca. 12.7 cm) long was bonded to a horizontal target substrate surface of a clean paper at least 12.7 lineal cm in firm contact. A 2 kg hard rubber roller was used to apply the strip. The free end of the coated strip was doubled back nearly touching itself so the angle of removal was 180°. The free end was attached to the adhesion tester scale. The tested paper test was well attached to the steel plate, which was clamped in the jaws of a tensile testing machine Zwick. The tape was peeled from the paper surface at a constant rate 300 mm per minute. The result was reported as the average of three tests.

The shear stress test allows to determine the PSA ability to maintain its position when shearing forces are applied. The measurement is performed using adhesive-coated strip applied to a standard stainless steel panel so that a 1inch x 1inch (ca. 2.5 cm x 2.5 cm) strip surface is in contact with the panel, and the other strip end being free. The steel panel with the coated strip attached was held in a rack, thus 180° angle between attached and free ends was formed. Subsequently, the latter was loaded with a hanging weight. The time necessary to separate the tape from the test panel was 4 h. The shear strength at 20°C and 70°C was measured according to AFERA 4012. The acrylic/CMS PSA coated tape was placed to a vertical standard stainless steel panel (maintaining standard contact area). To the free end of adhesive tape the load between 5 and 90 N (tested at 20°C) and between 5 and 40 N (tested at 70°C) was placed (Fig. 3).

SAFT (Shear Adhesion Failure Temperature) test is a modification of the shear-resistance and shear adhesion failure test. The samples were attached to the steel panel, and the free end was weighted down using a 10 or 5 N load. Next, the measuring system is placed into the test chamber. The temperature in

the chamber raised 2°C/min from ambient up to 225°C. The temperature at which the adhesive layer failed was noted (shear adhesion failure temperature -SAFT); this temperature value allows to evaluate the thermal performance of the adhesive.

Solubility in water of acrylic PSA containing CMS with various DS was tested at three pH values (7, 9 and 11) at 20°C using double-sided tape sample. For this test 10 cm² tape was stirred at 200 rpm in 150 mL of water medium with adjusted pH. The adhesive was green in color and the solubility time was evaluated visually, when the water medium turned green and no visible green spots on paper carrier was noticed.

Bleeding tendency test is required in paper industry, and qualitatively measures the tendency of applied adhesive to bleed through a paper sheet under pressure at elevated temperature. The strips of double-sided splicing tape were placed between the paper sheets. Subsequently, several paper sheets were added on both sides, and such a sample was placed in a platen press (100 N/cm²) at 40°C for 7 days. If the tested adhesive slightly bleeds the first paper sheet and no adhere to the second one – the bleeding is assessed as “slight” and adhesive is considered acceptable. Less desirable, but still acceptable is when the adhesive penetrates through the first sheet and adheres only slightly to the second one. Unsatisfactory, adhesive bleeds through the paper sheet and adheres tightly to the other. The bleeding tendency tests were performed for fax, newsprint, photographic and art paper.

2.2.6. Characterization of papers

The 3D topography of tested papers were conducted with laser scanning microscope VK9700 (Keyence, Japan). The microscope was equipped with a short wavelength (408 nm) laser light source and a pinhole confocal optical system. During LSM analysis the field of the microscope was scanned using a laser beam and an X–Y scan optical system. A light reflected from each pixel in the field of view was detected by the light receiving element. While moving the objective lens in the Z-axis and repeatedly scanning the measured area the reflecting light intensity based on the Z position was obtained. During the measurements the magnification of 400x was applied. The LSM film roughness (R_a and R_z) was calculated as the average of three profiles with the interval of 20 µm using the VK Analyzer software. The R_z values were determined as sum of the height of the highest profile peak and the depth of the deepest profile valley within an individual measuring distance, whereas R_a was the arithmetical mean value of the amounts of the ordinate value within an individual measuring distance.

The FTIR measurements of paper surface were performed as described in p. 2.2.1.

3. Results And Discussion

3.1. FTIR of carboxymethyl starch with various degree of substitution

The FTIR spectra of native potato starch and CMS with various degree of substitution were presented in Fig. 4. The special pattern, typical for native starch, in the region of 970 cm^{-1} and 1200 cm^{-1} was

preserved in CMS samples. The broad band between 3600 and 3000 cm^{-1} was attributed to O-H stretching (due to hydrogen bonding involving hydroxyl groups on the starch molecules) and at 2900 cm^{-1} to CH_2 symmetrical stretching vibrations; by carboxymethylation the intensity of both bands decreased (Spychaj et al. 2013). Importantly, the band of CMS carboxylate (-COO-) at ca. 1640 cm^{-1} could be observed which was the evidence of successful introduction of carboxymethyl groups into starch structure. Moreover, band in this region indicated that CMS was in (sodium) salt form as protonated –COOH gave signal at ca. 1730 cm^{-1} (Assaad and Mateescu 2010). The intensity of this band is attributed to carbonyl content (Kaczmarska et al. 2018). The CMS gave the strong bands at 1440 cm^{-1} and 1325 cm^{-1} characteristic for C-O-C bonds.

3.2. Prepared acrylic PSA

The synthesized basing water-soluble acrylic pressure-sensitive adhesive was characterized by the main parameters of viscosity, molecular weight and polydispersity which were presented in Table 1. The molecular weight of acrylic PSA is generally limited by the viscosity value - enabling to coat the adhesive on the substrate, but minimizing the amount of solvent necessary to evaporate (Paul 2011). The prepared acrylic copolymer exhibited M_n and M_w: 315 kD and 836 kD, respectively, and ca. 15 Pa·s viscosity. Importantly, soluble in water basing acrylic system has been synthetized.

Table 1
Main properties of synthesized acrylic pressure-sensitive adhesives

Viscosity [Pa•s]	M_w [Dalton]	M_n [Dalton]	$P_d = M_w/M_n$
15.2	836 000	315 000	2.66

3.3. Tack, peel adhesion and shear strength of synthesized water-soluble acrylic PSA containing carboxymethyl starch

The tack (Fig. 5) and peel adhesion (Fig. 6) of pressure-sensitive adhesive containing 5.0 wt.% CMS with various degree of substitution was tested using standard steel substrate as well as different commercial paper type: fax, newsprint, photographic and art paper.

The main adhesive properties, i.e. tack, peel adhesion and shear strength (cohesion) strongly depend on crosslinking (Zhang et al. 2020). Generally, the two former decrease with crosslinking density increase, whereas on the contrary, cohesion increases with crosslinking density (Czech 2003). The basic acrylic PSA was chemically crosslinked using 0.4 wt. % AlACA as crosslinking agent. This amount was selected basing on previous works as giving a balance between tack and adhesion on one side and cohesion on another (Czech 2005).

Despite the substrate type, introducing CMS into acrylic PSA beneficially affected the tack value, i.e. for steel (standard substrate) as well as for the used papers tack was higher than for basing PSA - for steel

increased from 11 N up to 14.4 N for PSA without and containing CMS with DS 0.86, respectively. The highest tack increase was reported for fax paper from 12.2 up to 16.1 N for PSA without and with CMS DS 0.86, respectively. The lowest tack increase was observed for photographic and art paper, which was probably the result of special finish and gloss characterizing these kinds of paper. They exhibit very smooth surface (roughness R_a 0.6 and 0.4 µm, R_z 11.9 and 3.5 µm, respectively – Table 2), which can observed in the 3D topography view in Fig. 7. Moreover, it could be noticed, that despite the paper type, the tack values increased with DS value of starch derivative. Thus, carboxymethyl groups introduced with CMS played an important role for tack improvement.

Table 2
Roughness values (R_z and R_a) of various paper types

Paper type	Roughness [µm]	
	R_z	R_a
Fax	39.784 ± 3.3	4.410 ± 0.23
Newsprint	33.399 ± 2.6	3.413 ± 0.25
Photographic	11.932 ± 1.4	0.603 ± 0.09
Art	3.537 ± 0.3	0.447 ± 0.06

It is known, that physical crosslinking via hydrogen bonds beneficially affects tack and peel adhesion (Czech 2003). Carboxymethyl starch molecules introduced into acrylic system could form hydrogen bonds between polar groups of CMS and acrylic chains. Similarly to reported formation of hydrogen bonds between starch and poly(acrylic acid) macromolecules (Biswas 2006). However, applying carboxymethylated derivative is more advantageous than native starch, as it exhibits lower tendency to retrogradation (Spycha et al. 2013).

The peel adhesion is an essential parameter for splicing tapes. The results of peel adhesion performed on steel (standard substrate) and on commercial papers revealed that with CMS addition the adhesion values increased by 3.6 N on steel, and within the same paper group increased by 3.9 N on fax, 3.8 N on newsprint, 3.6 N on photographic and 3.3 N for art paper, respectively. The adhesive properties depend strongly on the chain mobility (Zhang 2020). Carboxymethyl starch was mixed with chemically crosslinked acrylic system, thus CMS molecules maintained higher mobility than acrylic matrix. Additionally, within the same substrate type (steel or paper) the peel adhesion increased with CMS DS increase, what indicates that carboxymethyl groups importantly improved the performance of prepared PSA.

Considering the peel adhesion between various paper substrates it could be observed that for art paper noticeably higher peel adhesion values were reported. In case of photographic and art paper the special

paper finish was performed, which could affect adhesion. The FTIR spectra of tested papers (Fig. 8) revealed that their surface differ chemically. For fax and newsprint - cellulose was identified, and characteristic intensive band at ca. 3300 cm^{-1} attributed to OH groups was observed. The spectra of art and photographic paper were significantly different. For the former, the bands at ca. 700, 900 and 1400 cm^{-1} attributed to inorganic carbonate, were noted (Munawaroh et al. 2018). That indicated that calcium carbonate, i.e. one of the most popular paper filler (Hubbe and Gill 2016) was used for special paper finishing (responsible for low surface roughness – Table 2). However, its peel adhesion level for unmodified PSA was comparable with fax and newsprint paper. That could be the result of hydrogen bonding formation between adhesive's carboxyl groups and substrate's calcium carbonate (Jensen et al. 2018). In case of art paper the FTIR spectra was more complexed. Beside calcium carbonate absorption bands, special pattern for Si-OH (silanol) in a range 3600–3690 cm^{-1} as well as absorption bands typical for Al-O at ca. 540 cm^{-1} were observed. That revealed the presence of other common paper filler, i.e. kaolin (Krisnandi et al. 2018). Kaolin is the mineral composed mainly from kaolinite $Al_2Si_2O_5(OH)_4$, having Al-OH and Si-OH groups on the surface of clay lamellae (Silva E Silva 2017). Silanols participate in the formation of hydrogen bonds with H atoms and the electronegative atoms (e.g., oxygen atoms) (Zhao and Wan 2007). Moreover, hydrogen bonds could be formed via R-OH and carbonyls present on the paper surface as well (absorption bands at 1000–1100 cm^{-1} and ca. 1740 cm^{-1}, respectively). However, as the peel adhesion for art paper was noticeably higher when compared to other paper kinds it was probable that additional interaction between art paper surface and adhesive occurred. It is known that residual silanol groups can condense with the hydroxyl, alkoxy or carboxylic groups to form dimers or oligomers (Bilba and Arsene 2008; Gueyne and Seguin 1993). The enhanced adhesion to art paper was probably the result of condensation of silanol groups on paper surface with hydroxyl and carboxylic groups of adhesive.

Figure 9 shows the cohesive strength expressed by shear strength at 20°C and 70°C of PSA tapes with various carboxymethyl starch content and degree of substitution, using standard steel substrate. As it was expected, higher temperature negatively influenced the shear strength. The maximal shear strength 90 N at 20°C was noted for CMS 0.86, and dropped to 40 N at 70°C, respectively. Slightly increase of shear strength with degree of substitution value was observed. Moreover, increasing CMS content from 1 to 15 wt. % improved the shear strength. The additional shear strength SAFT test (Shear Adhesion Failure Temperature) has been performed on adhesive containing CMS with the highest DS at the temperature rising from 70°C up to 240°C - Fig. 10. In paper processing machine the paper transfer rate could be as high as 160 m/min and the temperature in a range 180–240°C (Czech and Malec 2006), thus evaluating the dynamic shear strength level is beneficial for potential use of prepared PSA in paper processing sector. For each CMS content the shear stress decreased with elevating temperature. It is a typical behavior, as during heating the polymer molecules gain the mobility, as a consequence gradually more lore loose structure is formed, and the cohesion drops dramatically. The best thermal properties and highest shear strength values were noted for 15 wt.% CMS content, ca. 500 N/2.5 cm at 70°C and ca. 150 N/2.5 cm at 240°C. The shear stress is strongly associated with the cohesion of adhesive material. Thus,

improved thermal properties of acrylic PSA with CMS 0.86 is probably the result of forming hydrogen bonds between polar CMS carboxylic and carbonyl groups of polyacrylate.

3.4. Solubility and bleeding of acrylic PSA containing carboxymethyl starch with various degree of substitution

In Table 3 the results of solubility time of based acrylic PSA and acrylic PSA with various CMS content were collected. Additionally, CMS with various degree of substitution was used. As solubilizing media water was used, and the alkali medium with pH 9 and pH 11. The latter was used as alkali solutions are commonly applied in paper industry.

Table 3
Solubility time of acrylic PSA containing CMS with various DS

Composition		Solubility time [s]		
		pH = 7	pH = 9	pH = 11
Basing acrylic PSA		502	373	256
PSA with CMS				
CMS	CMS content [wt. %]	pH = 7	pH = 9	pH = 11
DS 0.15	1	491	360	240
DS 0.60		480	350	232
DS 0.86		470	334	218
DS 0.15	3	480	328	210
DS 0.60		470	312	200
DS 0.86		451	292	185
DS 0.15	5	463	304	184
DS 0.60		431	282	163
DS 0.86		420	261	143
DS 0.15	7	443	286	159
DS 0.60		415	256	135
DS 0.86		398	240	116
DS 0.15	10	404	252	130
DS 0.60		360	229	110
DS 0.86		342	192	93
DS 0.15	15	360	213	102
DS 0.60		330	180	80
DS 0.86		314	152	60

Generally, all tested systems were completely soluble in water, and the filter paper carrier was water-dispersible. The water-solubility time values were very short, and did not exceed 9 min, which is the value qualifying for application in paper industry. The basic acrylic PSA dissolved in water in 8.4 min, and that was the longest dissolution time noted among the tested systems. Introducing CMS into acrylic PSA resulted in lowering the water dissolving time, and generally, the higher DS the shorter time was necessary

for complete dissolution: from 491s to 470 s for 1 wt. % CMS DS 0.15 and 0.86, respectively. Moreover, increasing the CMS content resulted in decreasing the water-solubility time, for DS 0.15: from 491 s to 360 s, for 1 wt. % and 15 wt.% content, respectively, and for DS 0.86: from 470 s to 314 s for 1 and 15 wt. % content, respectively. The carboxymethylation increased the hydrophilic character of starch, thus such a behavior of acrylic PSA with CMS was not surprising.

When comparing the solubility time at various pH values one could noticed that the solubility time significantly dropped at higher pH. It is known that protonated CMS exhibited reduced solubility in water, whereas in alkaline medium solubility is enhanced (Assaad and Mateescu MA 2010). Moreover, the tendency of lowering the dissolving time with DS increase could be noticed. The system based on acrylic PSA with 15 wt. % CMS DS 0.86 dissolved in 1 min at pH 11. Such short solubility time values qualify the acrylic PSA/CMS systems for application in paper industry.

The bleeding test allows to evaluate the adhesive tendency to penetrate through the paper. Moreover, it may bleed to the outer periphery and cause one paper layer stick to the other, which causes process problems in converting. After 1 week of bleeding tests no penetration of prepared acrylic PSA with CMS trough fax, newsprint, photographic, and art paper was observed. Thus, the obtained adhesives showed excellent resistance against bleeding. Bearing in mind short dissolving times in water and alkali, as well as no bleeding tendency additional application of acrylic PSA with CMS could be suggested, i.e. for water removable labels for packaging.

4. Conclusions

In this paper introducing biopolymer derivative – carboxymethyl starch into acrylic PSA has been described. CMS with various degree of substitution: from low up to highly substituted derivatives (0.15, 0.6, 0.86, respectively) were applied. The effect of DS on adhesive properties (tack, peel adhesion, shear strength) was tested using steel and various papers substrates: fax, newsprint, photographic, and art paper. The double-sided PSA tapes using water-dispersible filter paper carrier has been prepared. Moreover, as the tested adhesives were dedicated to the paper industry, the solubility rate in water and alkaline mediums as well as bleeding tendency test were performed. Despite the substrate type, introducing CMS into acrylic PSA beneficially affected the tack, peel adhesion and shear strength values. Generally, the higher DS of CMS applied the higher value increase of those parameters was noted.

Bearing all above in mind as well as excellent bleeding resistance allow to conclude that splice tape with acrylic PSA containing CMS with DS 0.86 could be potentially applied in paper processing industry.

Declarations

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Conflicts of interest

The authors declare no conflict of interest

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Authors contributions

Conceptualization: K. Wilpiszewska, Z. Czech; Methodology: K. Wilpiszewska, Z. Czech; Formal analysis and investigation: K. Wilpiszewska, Z.; Writing - original draft preparation: K. Wilpiszewska, Z. Czech.

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Figures

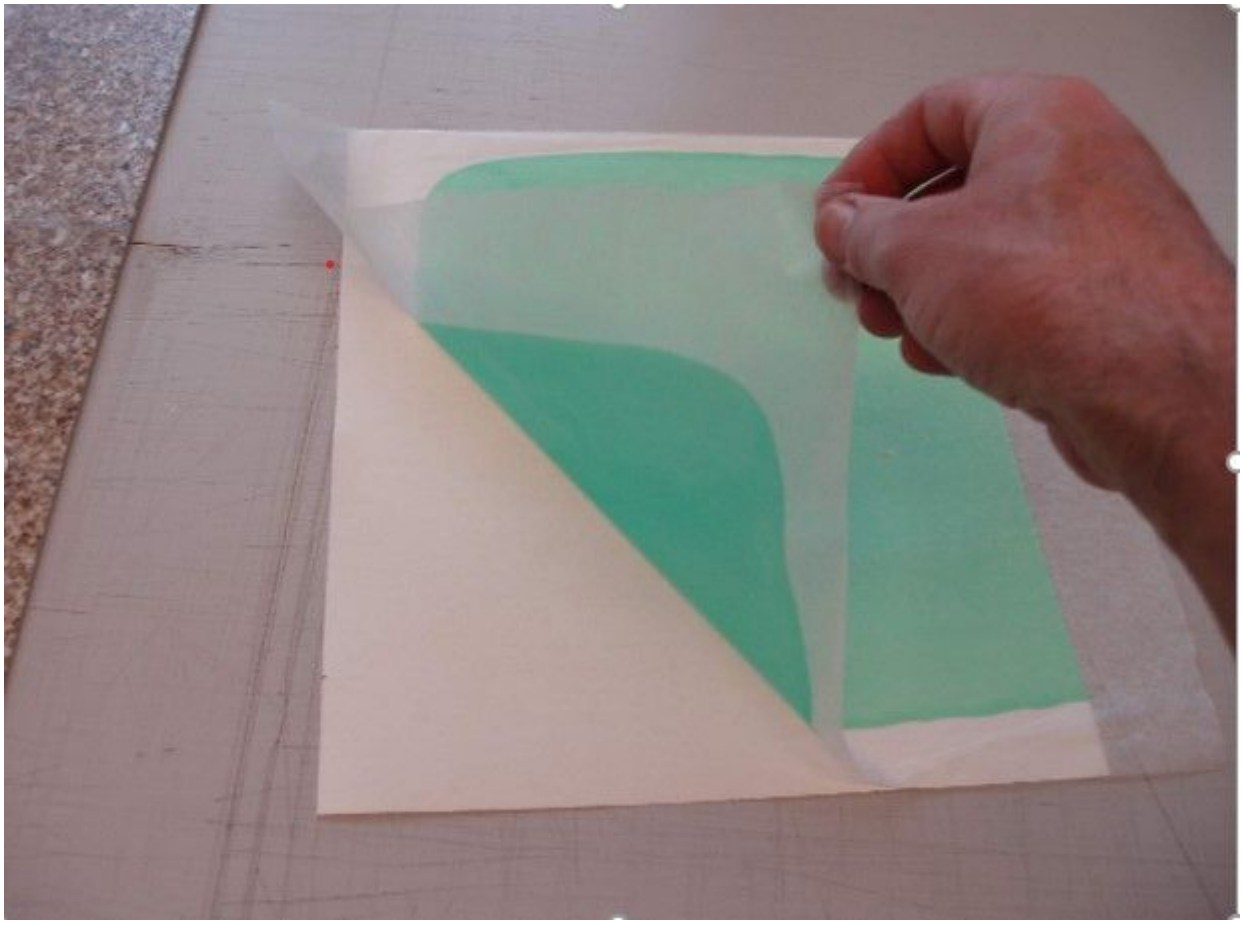

Figure 1

Prepared splicing tape (laboratory sample)

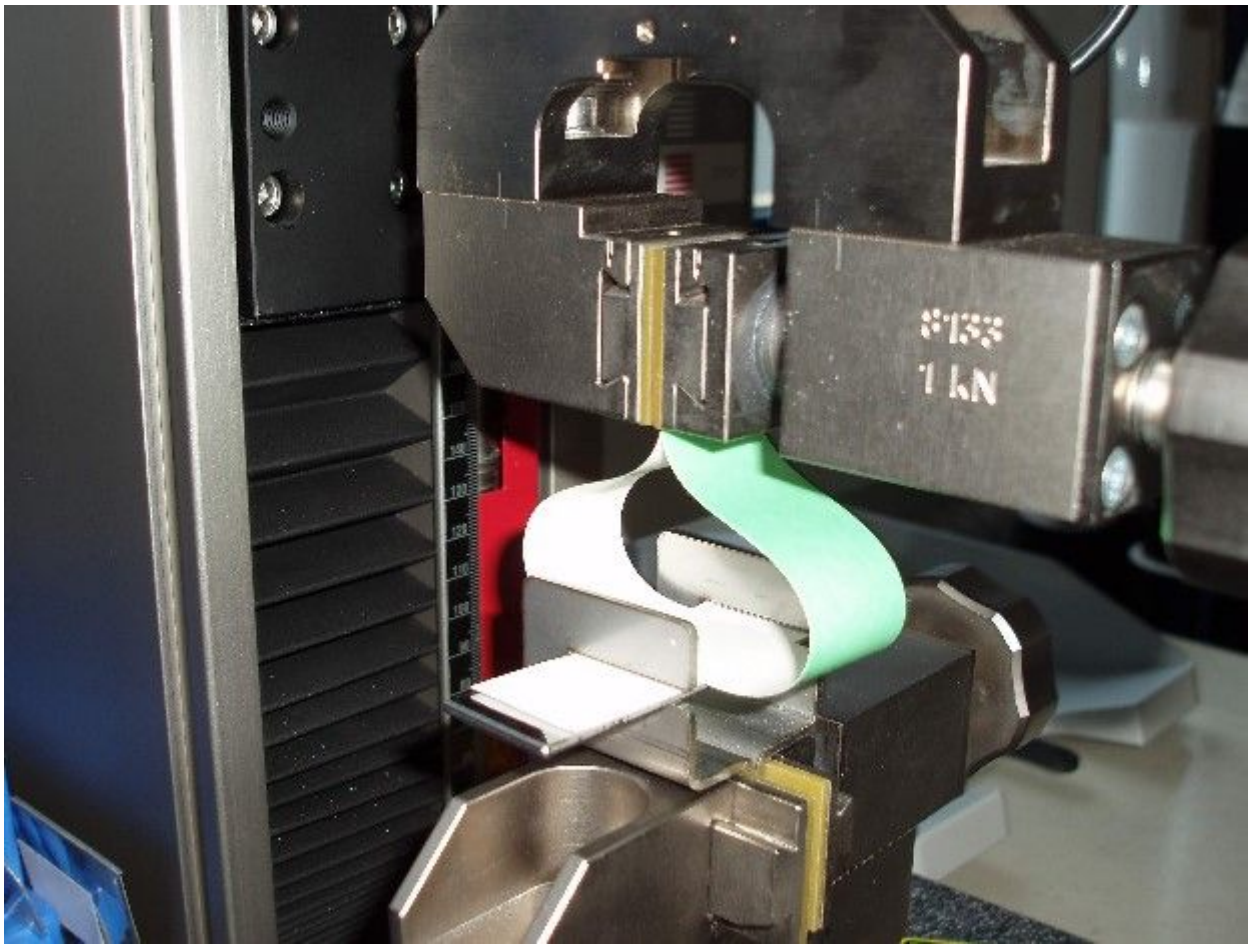

Figure 2

Loop tack on paper

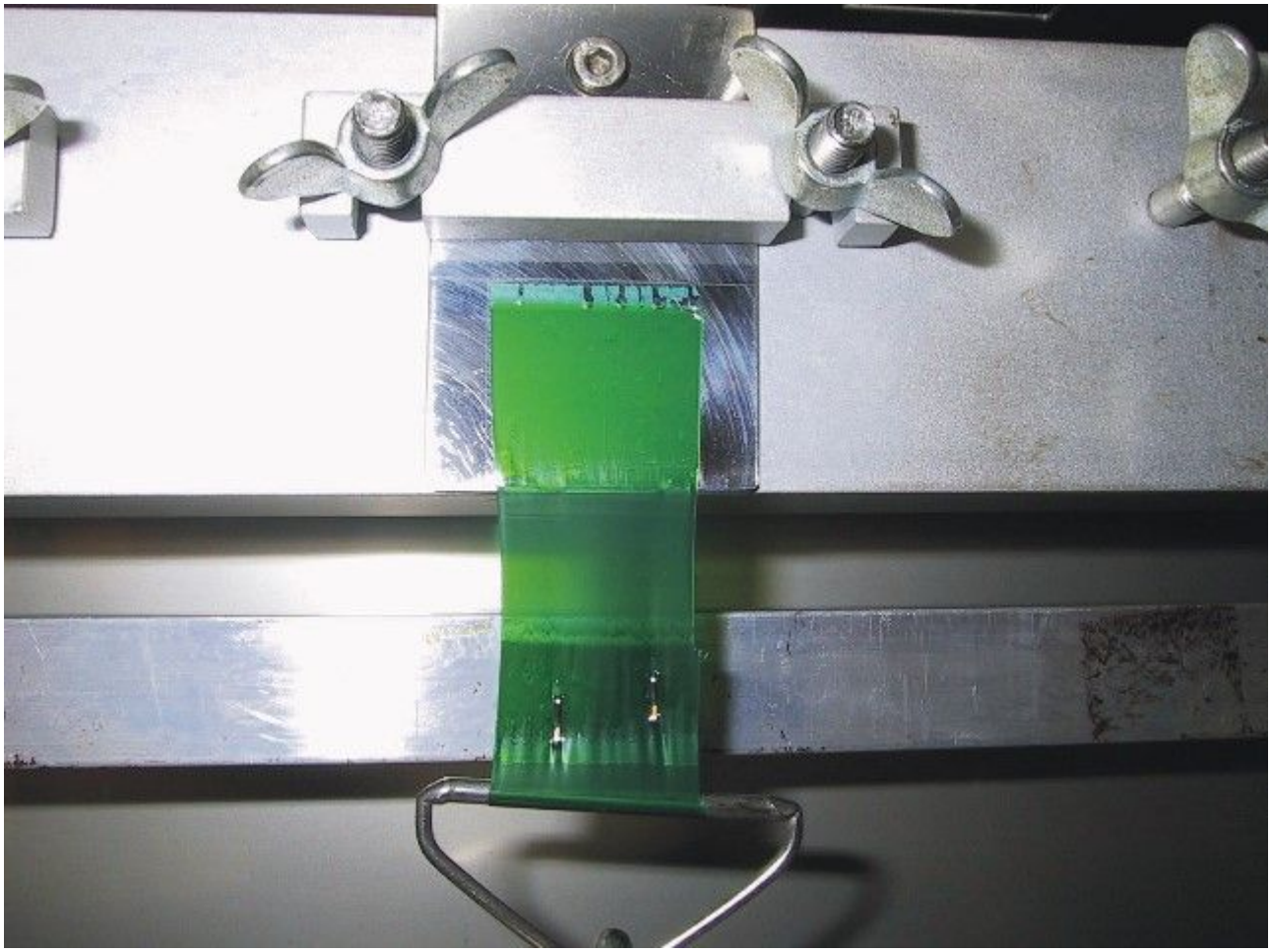

Figure 3

Shear strength test

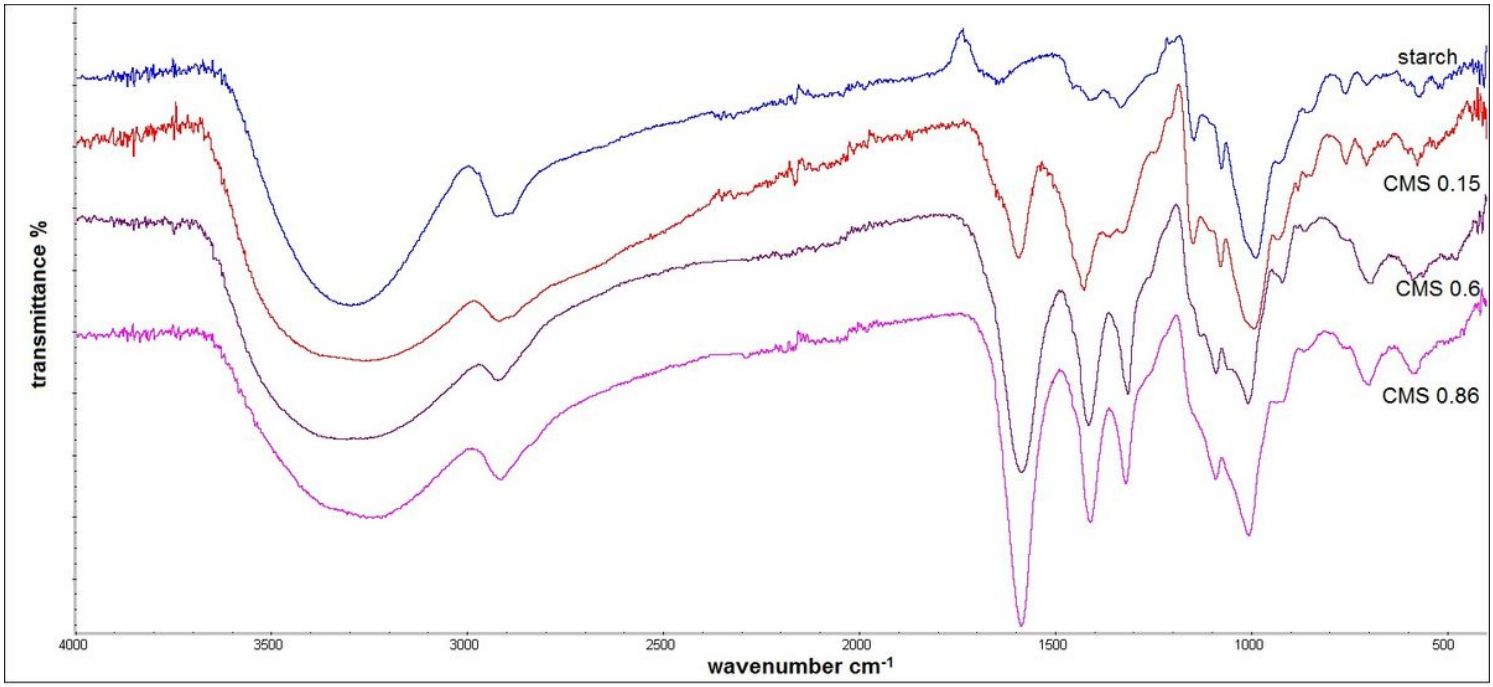

Figure 4

FTIR spectra of CMS with various degree of substitution and native starch

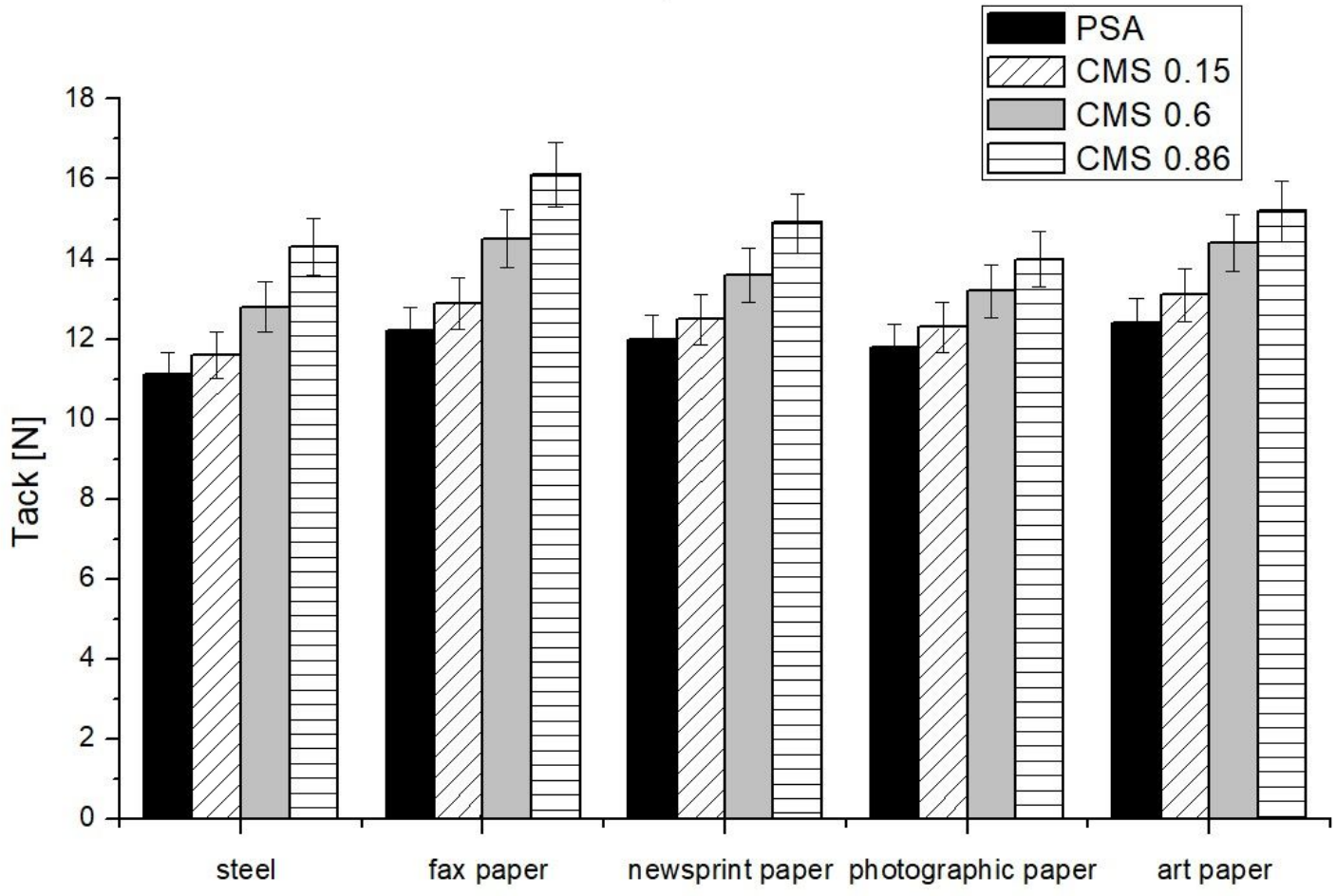

Figure 5

Tack of PSA containing 5 wt. % CMS with various DS

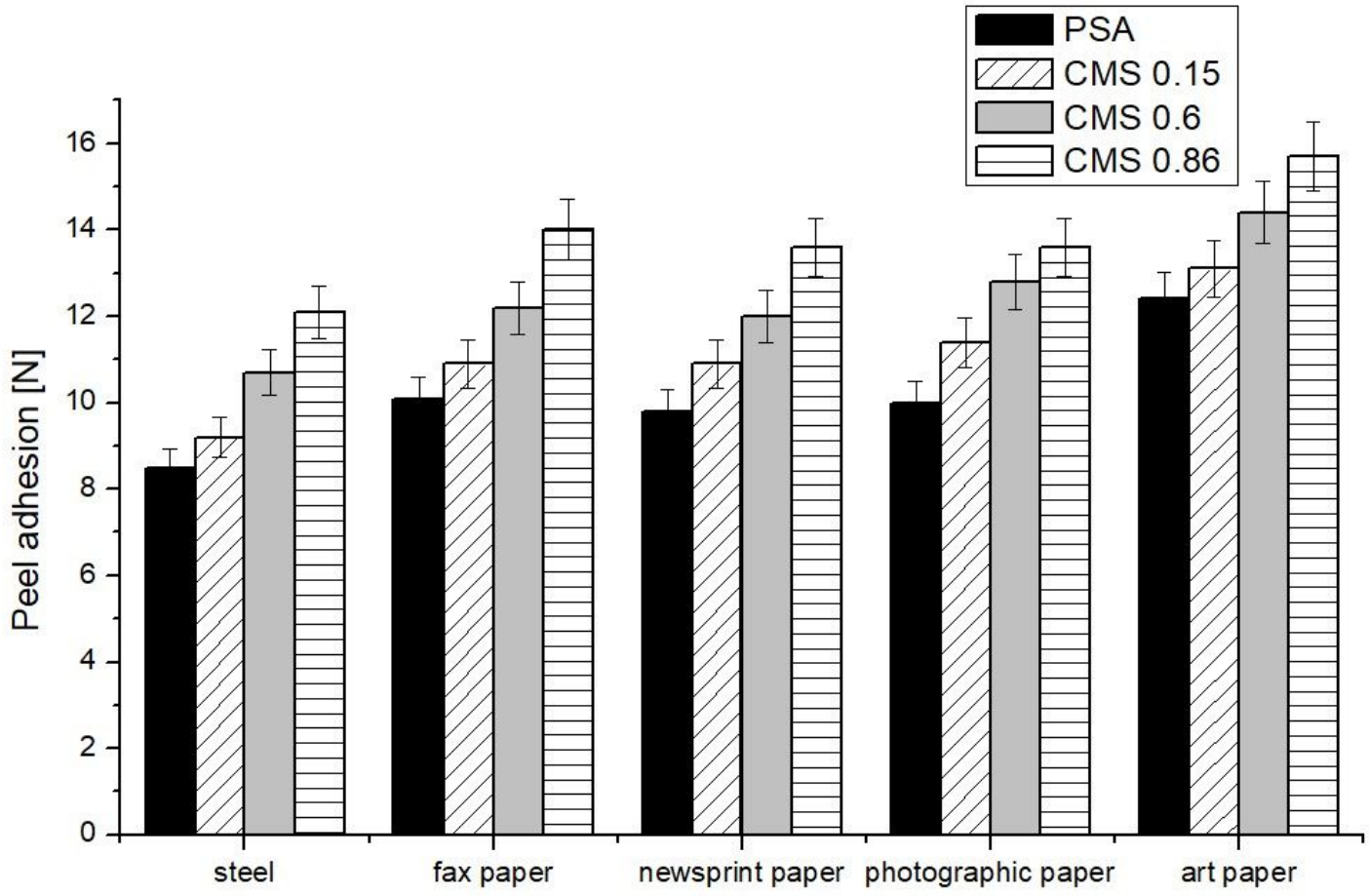

Figure 6

Peel adhesion of PSA containing 5 wt. % CMS with various DS

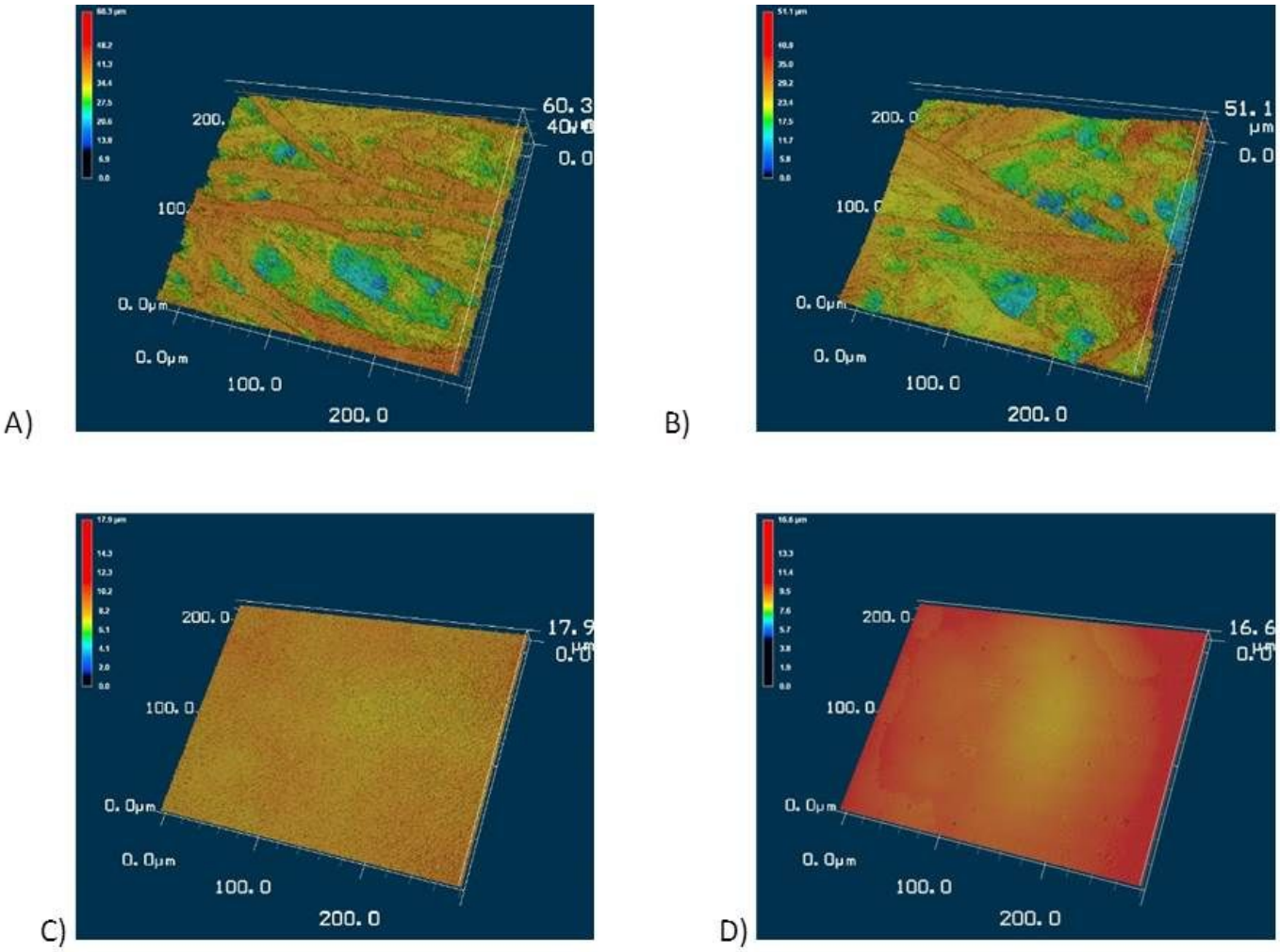

Figure 7

The 3D topographical view of: A) fax, B) newsprint, C) photographic, and D) art paper

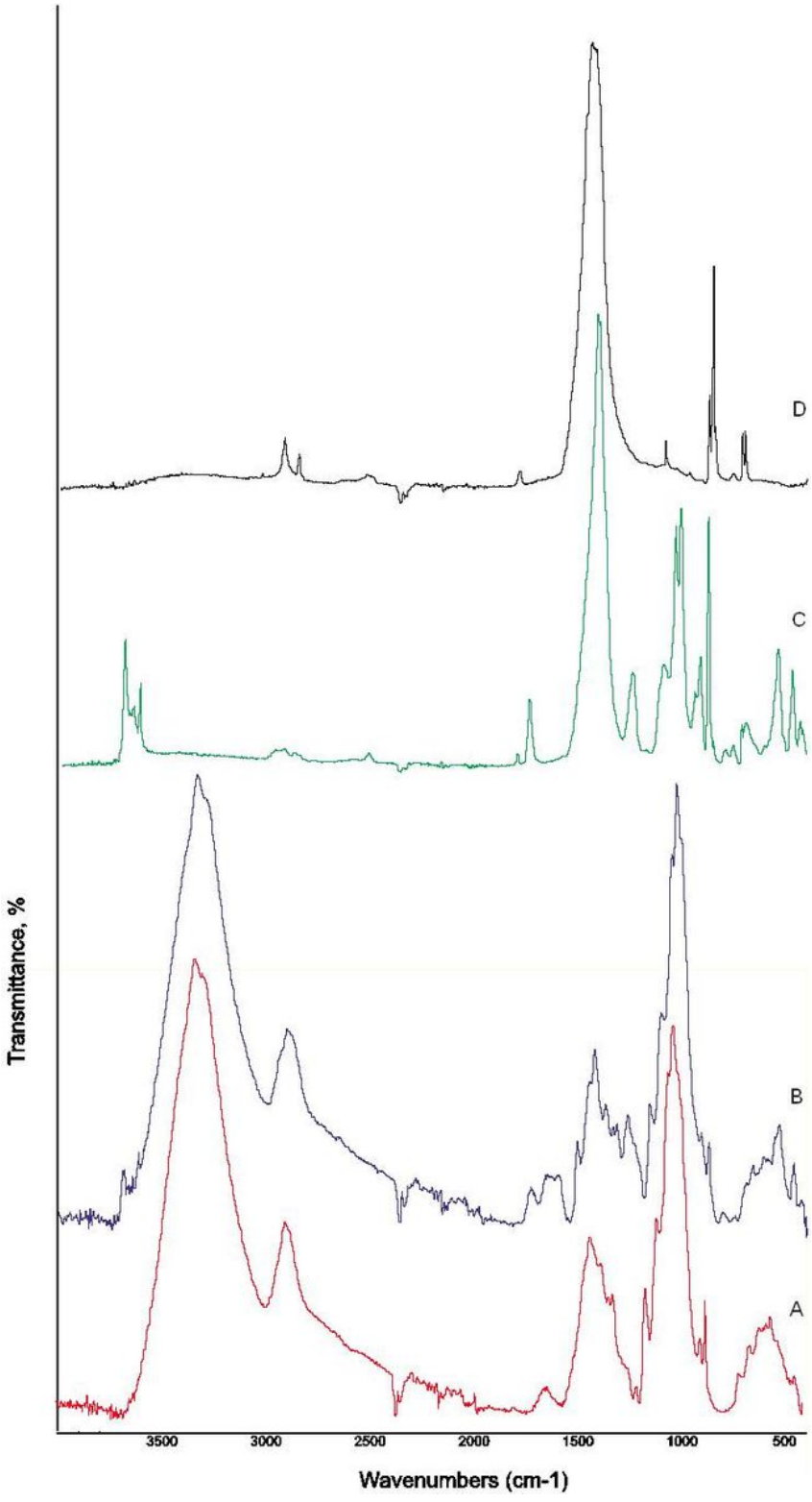

Figure 8

FTIR spectra of paper surface: fax (A), newspaper (B), art (C), and photographic (D) paper

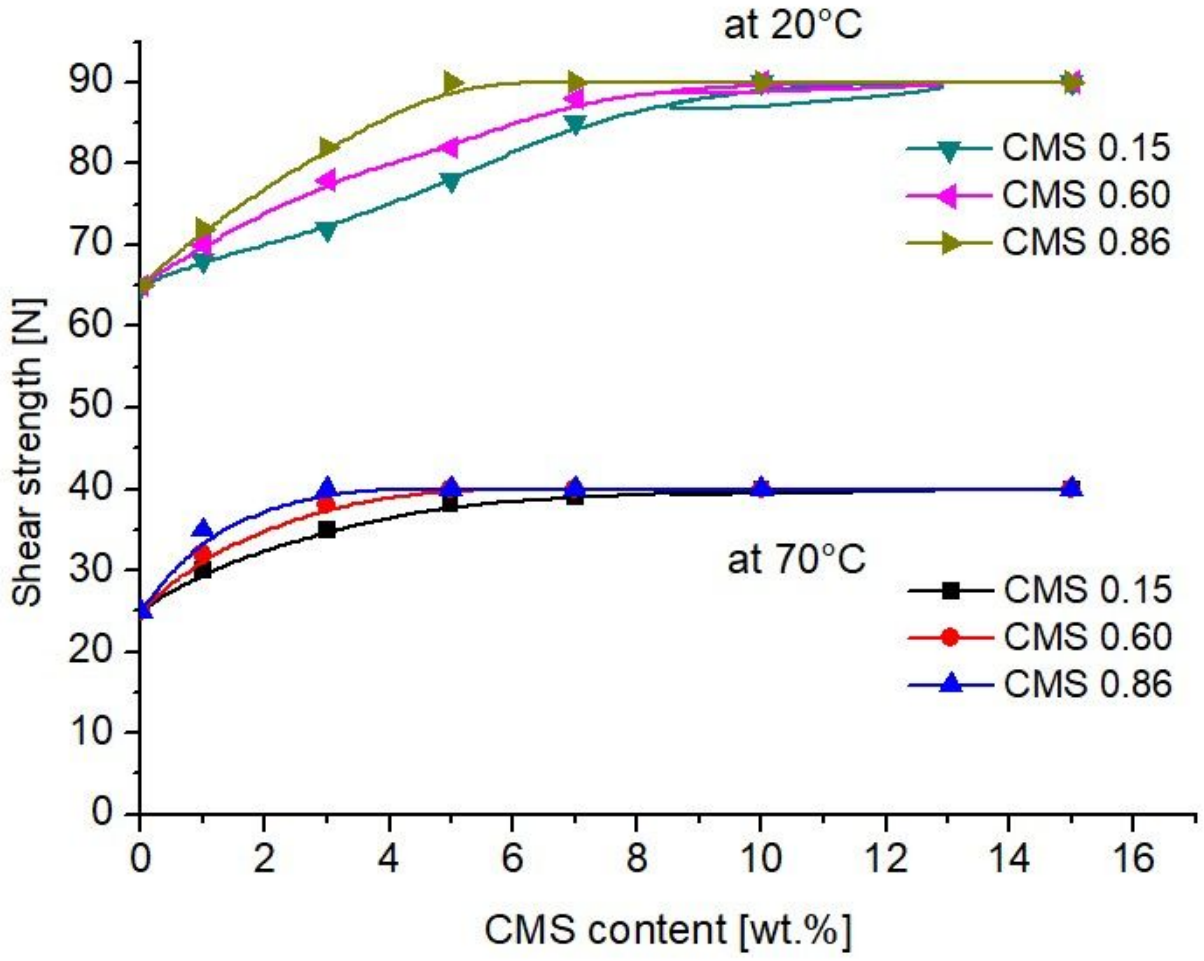

Figure 9

Shear strength at 20°C and 70°C as a function of CMS content in PSA system

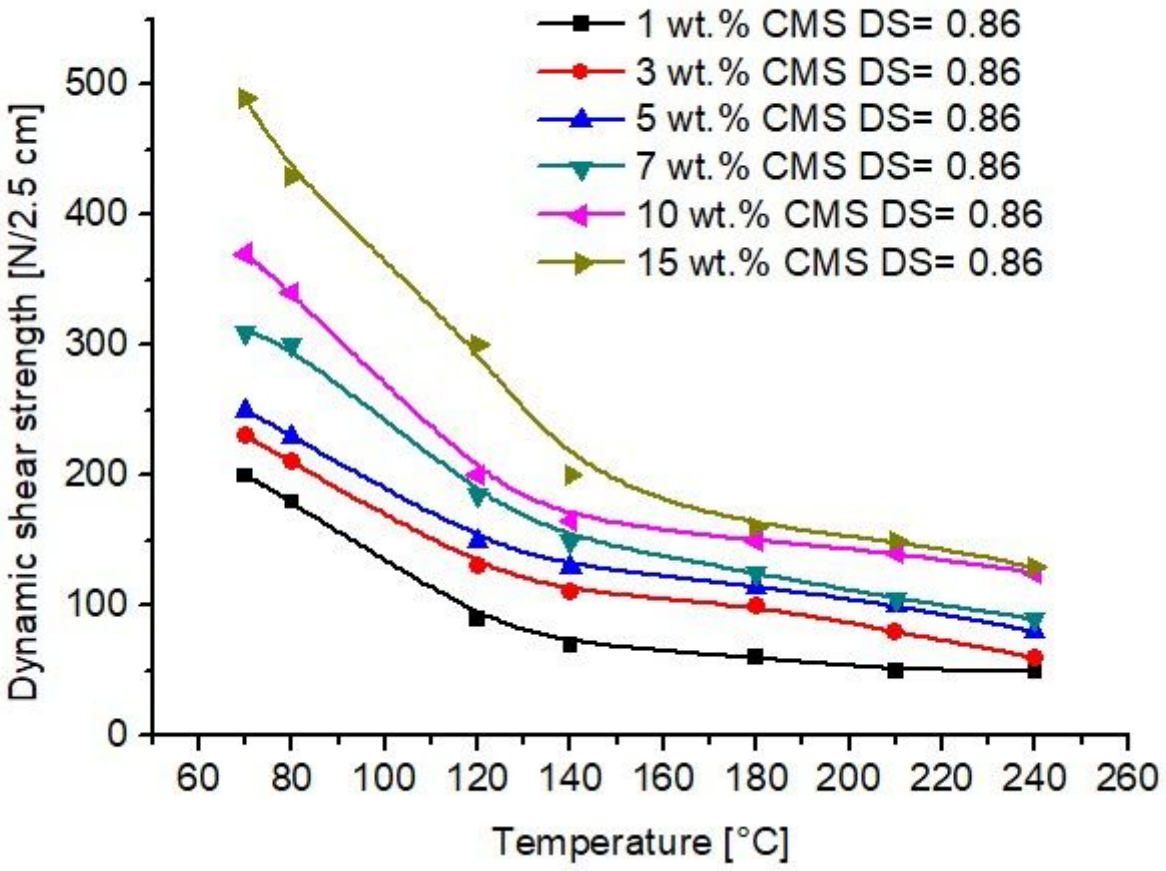

Figure 10

Shear strength results of the SAFT test