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

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Abstract A novel pressure-sensitive adhesive containing carboxymethyl starch (CMS) with various degrees of substitution, has been developed for the paper industry. Obtained adhesives were transferred onto water-dispersible paper carrier giving recyclable double-sided splicing tape. The effect of carboxymethyl starch degree of substitution (DS) on essential adhesive properties: tack, peel adhesion, as well as shear strength for steel and various papers have 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 parameter 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. The best performance exhibited the adhesive prepared from the mixture of acrylic monomers (35 wt% 2-ethylhexyl acrylate, 30 wt% butyl acrylate and 35 wt% acrylic acid), 0.4 wt% aluminum acetyl acetonate (crosslinking agent), 50 wt% poly(ethylene glycol) as plasticizer, and 15 wt% CMS with DS 0.86 (basing on acrylic polymer content).

Keywords Repulpable tapes · Carboxymethyl starch · Water-soluble · Pressure-sensitive adhesive

Introduction

Using water-soluble pressure-sensitive adhesive (PSA) is strongly recommended in the 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 roll 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 undesirable adhesive layer exposure, and in consequence sticking surface and paper folding. A 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 the cleaning process. However, the labels should remain on packaging when exposed to 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. 2018). In the case of pressure-sensitive adhesives addition of starch nanoparticles covered with acrylates (Zhang et al. 2018, 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 the paper processing industry were developed. The tapes consist of two main components: adhesive and carrier. The adhesive was water-soluble acrylic PSA containing carboxymethyl starch (CMS) with various degrees of substitution (DS). The water-dispersible filter paper was used as a carrier. 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, depend on the average number of OH groups in a starch repeating unit substituted with carboxymethyl groups, i.e. its degree of substitution (DS). An excellent film-forming ability of highly substituted CMS has been described (Wilpiszewska et al. 2015).

Introducing CMS into the 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 determined. Moreover, solubility in water as well as in the alkaline solution of prepared adhesives containing CMS has been tested.

Materials and methods

Materials

Carboxymethyl starch with a 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 dihydrate (EDTA) of Sigma-Aldrich (Germany) were used.

The industrial 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 poly(ethylene 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.

Methods

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 30 g (13.6–14 wt% moisture) was etherified in 270 g of isopropanol/water (90.5/9.5 wt%) mixture 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. The 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. The reagents amounts and efficiency of starch carboxymethylation were collected in Table 1. The degree of substitution was measured according to the method described by Kessel (1985). The CMS sample was moisturized by 1 mL of ethanol and dissolved in 50 mL of distilled water. Subsequently, a buffer was added (NH₄Cl 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 CuSO₄ solution. After 15 min, the measuring flask was filled up with water and the whole content was filtered. The 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.

**Synthesis of water-soluble acrylic PSA and its characterization**

Into a 1-liter reactor equipped with a thermometer, mechanical stirrer, water cooler, and dropping funnel the polymerization medium (solvent mixture 60 wt% ethyl acetate and 40 wt% acetone) was placed. The mixture of monomers (35 wt% 2-ethylhexyl 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 residual monomers was 4 h, and the polymer content after the polymerization process was 40 wt%.

The viscosity of the synthesized solvent-based acrylic pressure-sensitive adhesives was determined using Rheomat RM189 from Rheometric 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 10exp6 Å column from Hewlett Packard.

**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, at room temperature, 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 weeks of storage.

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

**Characterization of double-side splicing tapes**

The resulting adhesives were investigated for typical PSA properties, such as tack, peel adhesion, and shear strength by standard AFERA (Association des Fabricants Européens de Rubans Auto-Adhésifs) 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 can be conducted using common tensile strength test machines. The 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 inches (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 measuring tack using a 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 1 inch (ca. 2.5 cm) wide and about 5 inches (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 of 300 mm per minute. The result was reported as the average of three tests.

The shear stress test allows determining the ability of PSA to maintain its position when shearing forces are applied. The measurement is performed using an adhesive-coated strip applied to a standard stainless steel panel so that a 1 inch x 1 inch (ca. 2.5 × 2.5 cm) strip surface is in contact with the panel, and the other strip end is free. The steel panel with the coated strip attached was held in a rack, thus the 180° angle between attached and free ends was formed. Subsequently, a hanging weight was loaded. The time necessary to separate the tape from the test panel was 4 h. The shear strength at 20 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 a 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 ca. a 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 a 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 a paper carrier were noticed.

A bleeding tendency test is required in the 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 does not 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, the 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.

Characterization of papers

The 3D topography of tested papers was 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, a magnification of 400× was applied. The LSM film roughness (Rₐ and Rₚ) was calculated as the average of three profiles with an interval of 20 μm using the VK Analyzer software. The Rₐ values were determined as a sum of the height of the highest profile peak and the depth of the deepest profile valley within an individual measuring distance, whereas Rₚ was the arithmetical mean value of the amounts of the ordinate value within an individual measuring distance.

The FTIR measurements of the paper surface were performed as described in section "Synthesis of medium and high substituted CMS and their characterization".

Results and discussion

FTIR of carboxymethyl starch with various degrees of substitution

The FTIR spectra of native potato starch and CMS with various degrees of substitution were presented in Fig. 4. The special pattern, typical for native starch, in the region of 970 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 CH₂ 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 evidence of the successful introduction of carboxymethyl groups into a starch structure.
The intensity of this band increased with the degree of substitution. Moreover, the band in this region indicated that CMS was in (sodium) salt form as protonated –COOH gave a 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 absorption bands at 1440 and 1325 cm\(^{-1}\) characteristic for C–O–C bonds, and their intensity depended on the degree of starch modification.

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 2. 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, a water-soluble acrylic system has been synthesized.

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 adhesives containing 5 wt% CMS of various degrees of substitution, were tested using standard steel substrate, and different commercial paper types: 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, tack and peel adhesion decreased 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 a crosslinking agent. This amount was selected based on previous works as giving a balance between tack and adhesion on one side and cohesion on another (Czech 2005).

Introducing CMS into acrylic PSA beneficially affected the tack value, i.e. for steel (standard substrate), and the used paper tack was higher than for basing PSA—for steel increased from 11 N up to

| Viscosity (Pa s) | \(M_n\) (Dalton) | \(M_w\) (Dalton) | \(P_d = M_w/M_n\) |
|-----------------|-----------------|-----------------|-----------------|
| 15.2            | 836 000         | 315 000         | 2.66            |
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 surfaces (roughness $R_a$ 0.6 and 0.4 μm, $R_z$ 11.9 and 3.5 μm, respectively—Table 3), which can be observed in the 3D topography view in Fig. 7. Moreover, it could be noticed, that despite the paper type, the tack values increased with the DS value of starch derivative. Thus, carboxymethyl groups introduced with CMS played an important role for indicatesthat carboxymethyl in tack improvement.

It is known, that physical crosslinking via hydrogen bonds beneficially affects tack and peel
adhesion (Czech 2003). Carboxymethyl starch molecules introduced into the 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 et al. 2006). However, applying carboxymethylated derivative is more advantageous than native starch, as it exhibits a lower tendency to retrogradation (Spychaj et al. 2013).

The peel adhesion is an essential parameter for splicing tapes. The results of peel adhesion performed on steel (standard substrate) and 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

| Paper type   | Roughness (µm) |   |
|--------------|----------------|---|
| Fax          | 39.78±3.3      | 4.41±0.23 |
| Newsprint    | 33.39±2.6      | 3.41±0.25 |
| Photographic | 11.93±1.4      | 0.60±0.09 |
| Art          | 3.53±0.3       | 0.44±0.06 |

Table 3 Roughness values (Rz and Ra) of various paper types

![Fig. 7](https://example.com/fig7.png)

Fig. 7 The 3D topographical view of: A fax, B newsprint, C photographic, and D art paper
newsprint, 3.6 N on photographic and 3.3 N for art paper, respectively. The adhesive properties depend strongly on chain mobility (Zhang et al. 2020). Carboxymethyl starch was mixed with a chemically crosslinked acrylic system, thus CMS molecules maintained higher mobility than the acrylic matrix. Additionally, within the same substrate type (steel or paper) the peel adhesion increased with CMS DS increase, which 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 the 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 differs chemically. For fax and newsprint—cellulose was identified, and a 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 art paper, 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 fillers (Hubbe and Gill 2016) was used for special paper finishing (responsible for low surface roughness—Table 3). 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 carboxyl groups of adhesive and calcium carbonate of the substrate (Jensen et al. 2018). In the case of art paper, the FTIR spectrum was more complex. Besides calcium carbonate absorption bands, the special pattern for Si–OH (silanol) in a range of 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 $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, having Al–OH and Si–OH groups on the surface of clay layers (Silva et al. 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 carboxyls present on the paper surface as well (absorption bands at 1000–1100 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 Arsen 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.

**Fig. 8** FTIR spectra of paper surface: fax (A), newspaper (B), art (C), and photographic (D) paper
Figure 9 shows the cohesive strength expressed by shear strength at 20 and 70 °C of PSA tapes with various carboxymethyl starch content and degree of substitution, using standard steel substrate. As was expected, higher temperatures 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 the 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 a 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 the potential use of prepared PSA in the paper processing sector. For each CMS content, the shear stress decreased with elevating temperature. It is typical behavior, as during heating the polymer molecules gain mobility, as a consequence gradually more 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 CMS and polyacrylate chains. It is known, that poly(acrylic acid) forms intramolecular hydrogen bonds between carboxyls as well as with hydroxyls present in the polymeric system (Chen and Zhang 2010; Khutoryanskaya et al. 2014). The formation of hydrogen bonds could be detected by FTIR spectroscopy, e.g. the absorption of O-H···O bond is shifted to lower frequencies since its strength is weakened when compared to non-hydrogen bonded O–H group (Nakamoto et al. 1955). In Fig. 11 the FTIR spectra of PSA, and PSA with CMS (low and high DS), in a range attributed to hydroxyls and hydrogen bonds formation, i.e. 3000–3700 cm⁻¹ (Grabowska and Kaczmarska 2014), was presented. The absorption band (determined as a local minimum) shifted from 3398 to 3354 cm⁻¹, for PSA and adhesive containing CMS 0.86, respectively, indicating intermolecular hydrogen bond formation.

Solubility and bleeding of acrylic PSA containing carboxymethyl starch with various degrees of substitution

In Table 4 the results of solubility time of based acrylic PSA and acrylic PSA with various CMS content were collected. Additionally, CMS with various degrees of substitution was used. Water was used as solvent, and the alkali medium with pH 9 and pH 11. High pH was used as alkali solutions are commonly applied in the paper industry.
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 the paper industry. The basic acrylic PSA dissolved in water within 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 491 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 to 360 s, for 1 and 15 wt% content, respectively, and for DS 0.86: from 470 to 314 s for 1 and 15 wt% content, respectively. The carboxymethylation increased the hydrophilic character of starch, thus such behavior of acrylic PSA with CMS was not surprising.

When comparing the solubility time at various pH values one could notice 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 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 evaluation of the adhesive tendency to penetrate through the paper. Moreover, it may bleed to the outer periphery and cause one paper layer sticks to the other, which causes process problems in converting. After 1 week of bleeding tests no penetration of prepared acrylic PSA with CMS through 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.

Conclusions

In this paper introducing biopolymer derivative – carboxymethyl starch into acrylic PSA has been
described. CMS with various degrees 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, newprint, photographic, and art paper. The double-sided PSA tapes using a water-dispersible filter paper carrier have 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 tests 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 the above in mind as well as excellent bleeding resistance allows to conclude that splice tape with acrylic PSA containing CMS with DS 0.86 could be potentially applied in the paper processing industry.

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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.

Declarations

Conflict of interest The authors declare no conflict of interest.

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