Starch-Fatty Complex Modified Filler for Papermaking

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ABSTRACT

In order to improve filler-fiber bonding in paper, starch-filler composites were prepared by a starch-fatty acid complex formation method. These composites were used as a papermaking filler to improve the physical properties of the paper, filler retention, and the sizing effect. The solubility of the starch-fatty acid complex in water at different temperatures was measured. The results indicated that the starch-fatty acid complexes have very low solubility in water below 70°C, which can be easily coated on clay surface to modify clay-fiber bonding ability. The clay-starch composite filled handsheets showed that paper strength could increase more than 100~200% compared to untreated clay. It was found that ZDT of the handsheet decreased as the clay content increased when unmodified clay was used, but it increased when the starch-fatty acid composite modified filler was used. It was also found that the presence of fatty acids in the complex increased the water-repellant property of the handsheet, which can be used to aid in sizing during papermaking. Filler distribution and bonding characteristics between the composite and fiber were investigated using Scanning Electron Microscopy (SEM).

INTRODUCTION

The increase of filler content in paper has been driven by moves to reduce papermaking cost, improvements in optical properties, printability, and the water removal rate during papermaking. However, as filler loading is increased, paper strengths, bulk, and stiffness are usually decreased. To increase the proportion of filler without sacrificing paper properties, various methods such as preflocculation *(1-4)*, lumen loading *(5-7)*, chemically treated filler with polymer *(8,9)* and filler-wood fine composites *(10)* have been explored. Although many approaches have been studied for improving the paper strength at high filler contents, except for the preflocculation method, none of these technologies has delivered a practical solution to paper manufactures.

Traditionally, starch has been used in wet-end papermaking applications because of its relatively low price and its ability to improve paper strength. The mechanism of the increase in dry tensile strength using starch has been suggested. It is believed that starch adsorbs to wood fibers during wet end processing and thereby enhances bonding through the formation of hydrogen bonds *(11)*. Gaspar concluded that improvements in dry strength were due to increase in shear strength per unit bonded area (12). Although starch can improve the strength of paper, there are some problems related to high starch addition in wet end papermaking process. For example, the retention of raw starch in a pulp furnish is very poor, less than 40% (13). In order to enhance the adsorption of starch to anionically charged wood fiber surface, the cationic groups are usually introduced to starch's backbones. However, such chemical modification of starch significantly increases the cost of papermaking.

Although the adsorption of starch can be improved by introducing cationic groups, the retention of starch on wood fibers is still a problem when anionic trash in the wet end furnish is high, such as in ground wood pulps and recycled fibers. Furthermore, the saturation adsorption of cationic starch on fibers does not allow papermakers to further increase cationic starch amount beyond the saturation point in the papermaking wet end process. Therefore, the amount of starch on wood fibers is limited by its maximum adsorption amount. The positively charged starch may also cause fiber flocculation or over cationize the system if the amount of starch is too high. The poor formation and slow drainage caused by high starch addition are also practical problems in papermaking (14). If the retention of starch cannot be well controlled, unretained starch will accumulate in the whitewater and create pitch, slime, and sticky problems.

Recently, we reported a method for modification of precipitated calcium carbonate (PCC) or clay with coated starch (15, 16). The results indicated that the strength of PCC or clay filled sheets could be significantly improved if the filler surface was coated by starch. In this work, we report an easier and lower cost method for coating starch on filler for paper strength improvement.

To maximize the efficiency and reduce the papermaking problems using starch coated fillers, the starch coating layer should be water-insoluble at papermaking conditions. Insoluble or less soluble starches have been developed for a filling material or ion exchange resin. The precipitation of cooked starch using organic solvents such as alcohol or acetone or saline salts such as $MgSO_4$ and $(NH_4)_2SO_4$ is the most common way.

The crosslinking methods using aldehyde, vinyl sulfone, epichlorohyrin can also be used for preparation of water-insoluble starch.

In this study, the precipitation of starch was carried out through the formation of water-insoluble starch-fatty acid complexes in the presence of clay particles. Schoch and Williams reported that amylose could be precipitated by fatty acids in a microcrystalline condition *(17)*.

The mechanism of the complex formation between the starch and fatty acid was thought to be the formation of ester linkages in early days *(18)* but it is believed now that unbranched polar compounds, *e.g.*, fatty acids and their monoglycerides, form helical inclusion complexes with amylose under suitable conditions *(19, 20)*. These complexes are considered to be similar to the blue polyiodide complex of amylose whose structure had been originally elucidated by Rundle and Baldwin *(21)*. The complexed or guest molecule is thought to occupy the central axis of a helix consisting of 6, 7, or 8 glucosyl residues per turn, with a repeat spacing of 0.8 nm and internal cavity is considered to be a hydrophobic tube *(22, 23)*. The hydrophobic group of complexing agents can lie within the amylose helix and is stabilized by Van der Waal contacts with adjacent C-hydrogens of amlyose, while hydrophilic portions of the ligands are outside the helix. Further insertion of the fatty acid leads to steric conflicts because the steric and electrostatic repulsions prohibit the polar group from entering the cavity *(25)*.

In this study, different aggregates of clay-starch composites by starch-fatty acid complexation were prepared and characterized. The effects of clay-starch composites on paper properties were also investigated. Compared to our previous approaches, relatively larger starch ratio in clay-starch composites was used because of the simple operation process and the low solubility of starch prepared in this study.

EXPERIMENTAL

Materials

Dry Branch Kaolin Co., Inc. (Dry Branch, GA) provided the calcined kaolin clay. Raw corn starch was used for this experiment. Palmitic acid was obtained from Aldrich. Bleached hardwood and softwood pulps were each refined in a Valley beater to a freeness of 400 CSF. Equal proportions of the two pulps were mixed, and the mixture was used as the base pulp furnish for the handsheets. Cationic polyacrylamide (Percol-175) for filler retention was obtained from Ciba Specialty Chemicals. Cationic starch (STA-LOK 400) for filler retention and dry-strength was procured from Tate & Lyle Ltd (Decatur, IL).

Preparation of clay-starch composites

The composite with clay to starch ratio of 1:1 was prepared as the follows: 5g of clay was added to 3% uncooked raw corn starch suspension that contained 5g of dry weight starch. The mixture then was stirred and cooked at 95°C for 30 minutes. 0.5g of palmitic acid was added to cooked starch-clay suspension and the mixture was then adjusted to pH 11 by 0.01M KOH. After stirring for 10 minutes, the cooked clay-starch mixture was poured into 0.01M HCl solution to neutralize it. The complex was then precipitated by adding a few drops of 2M HCl to pH 5 with 200rpm stirring speed. The resultant composites were directly used for handsheet making. The two different palmitic acid ratios (10% and 30%) based on the solid starch were compared.

Characterization of clay-starch composites by starch-fatty acid complex

The morphology and surface analysis was performed by SEM. Swelling and solubility of starch measured at different temperatures were determined using the method described previously *(16)*. For the solubility measurement of starch, the wet clay-starch composite (2g) collected after filtration and washing was agitated in 50g of distilled water for 30 minutes under each different temperatures. The suspension was cooled to 20°C, then was poured into pre-weighed centrifuge tubes and centrifuged at 3000 rpm for 10 minutes. The supernatants containing dissolved starch were gathered and tested by measuring total organic content (TOC) using Shimadzu Total Organic Analyzer 5050. At this time, the supernatants were removed thoroughly, and then the remaining sediments were weighed to determine swelling power. The weighed sediments were dried in vacuum dryer for 24hours. The swelling power was obtained from weighing sediments before and after drying. The solubility and the swelling power were defined as follows;

$$\text{Solubility (\%)} = \frac{\text{wt. of initial dry starch - wt. of dry starch not dissolved}}{\text{wt. of initial dry starch}} \times 100$$

$$\text{Swelling power} = \frac{\text{wt. of wet starch after centrifuge}}{\text{wt. of starch after drying}}$$

In order to characterize the structure of the starch-fatty acid complex, X-ray diffraction was analyzed as follows: Powdered samples (pulverized to pass 150mess) were equilibrated at 23°C and 45% relative humidity for 2 days prior to analysis. X-ray diffractometer (PW 1800, Philips Co. Ltd., USA) was operated at 40kV, 30mA. Diffractograms were obtained from 10° 2θ to 40° 2θ with a scanning speed of 0.04°/second and scanning step of 0.05° 2θ.

The measurement of composite size was performed using a commercially available canning laser microscope (Lasentec Corporation, Redmond, WA, USA). The effect of pH and shear force on composite formation was investigated from measuring the composite size using this technique. The detail mechanism and operation method of FBRM is described elsewhere (26).

Handsheet preparation and determination of paper properties

Bleached hardwood and softwood pulps were each refined in a Valley beater to a freeness of 400CSF. Equal proportions of the two pulps were mixed, and the mixture was used as the base pulp furnish for the handsheets.

The pulp was diluted to 0.5 wt% and various amounts of the composite aggregates were added during the handsheet formation. After the addition of the composites, the slurry was stirred for 20s at 700rpm without adding any retention aids. Handsheets with a target basis weight of 60g/m^2 were prepared according to TAPPI Test Method T 205 "Forming Handsheets for Physical Tests of Pulp". The control handsheets were prepared using unmodified clay with 0.05 – 0.1wt% cationic polyacrylamide(CPAM) retention aid (based on dry fiber weight). For comparison of the composite with conventional wet-end system, the cationic starch was cooked at 90°C for 2 hour, then directly added into the pulp slurry during the handsheet formation. After wet pressing twice at 50psi for 5 and 2 minutes respectively, all handsheets were dried at 105°C for 7 minutes on the Emerson Speed Dryer (Model 130). The physical properties of the paper were measured according to the standard TAPPI methods T220, T494, and T541. The filler content was determined by ashing the paper in a muffler oven according to the standard TAPPI method T211. The contact angle was measured using First Ten Angstroms 32 contact angle analyzer (Portsmouth, Virginia) equipped with a precise stepper motor driven syringe pump and a video camera. The wettability of handsheets was calculated by TAPPI method T458:

Rate of change of wettability (R) = Change of contact angle / change of time

RESULTS AND DISCUSSION

Starch-fatty acid complex formation

In order to investigate the complex formation and the coating efficiency of starch-clay composites, the starch and palmitic acid mixture at different ratios without adding clay were first investigated. The cooked starch and palmitic acid were mixed at pH 11 then neutralizing to pH 5 to form water-insoluble complexes. After separation of the insoluble complex by sedimentation, the amount of the starch left in the supernatant was analyzed by TOC, and the results are shown in Figure 1. It can be seen that the soluble starch amount dramatically decreased as the molar ratio of palmitic acid to starch increased. At molar ratios of greater than 0.07, the soluble starch amount was less than 0.3%, which means almost >99% of starch was precipitated.

The effect of the fatty acid ratio on the formation of the complex formation was also investigated using X-ray diffraction. X-ray diffraction scans of starch-fatty acid complexes at different palmitic acid ratios are shown in Figure 2. The spectrum indicated a maximum at 2θ=19.8°, which became apparent when the palmitic acid to starch ratio is greater than 0.3. The maximum at 2θ=19.8° presents V-type inclusion complexes of amylose *(27)*.

In contrast with the starch-fatty acid complex, only the amorphous structure without any crystalline peaks was observed for pure cooked starch. Therefore, the reduction of solubility of starch is believed to be caused by the crystalline structure of starch-fatty acid complex. As the fatty acid ratio increased above 0.3, two peaks at 21.4° and 23.8° were also observed. These peaks reflect the presence of a pure crystalline fatty acid *(28)*.

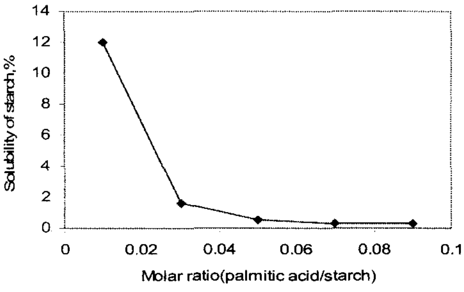


Fig. 1. Change of soluble starch amount with different molar ratios of palmitic acid to starch in the complex.

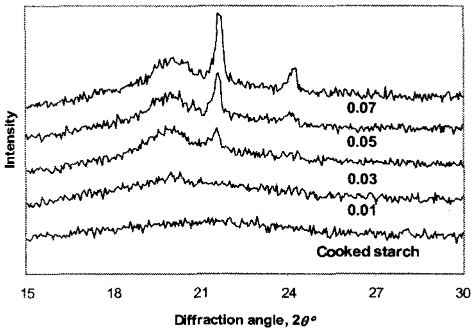


Fig. 2. X-ray diffractions of starch-palmitic acid complexes at different ratios of palmitic aicd to starch.

Starch-fatty acid-clay composite formation

The clay-starch composite was prepared by precipitation of starch-fatty acid complexes on the clay surfaces. In the experiments, required amounts of clay, starch, and palmitic acid were mixed and cooked together at pH 11. The cooked mixture (6.5% total solid concentration) was then poured into 0.01M HCl solution (the same volume as the cooked mixture) to be neutralized while stirring at 200 rpm. As soon as the shear forces were stopped, the white composites were formed quickly within 20 seconds and precipitated out from the solution.

The solubility of this coated starch in water at papermaking conditions will be a critical issue for real application.

If the solubility of coated starch in water is high, the structure of composite will be disrupted and the clays in composite aggregates will be separated to individual particles. Furthermore, the high solubility of starch complex will cause many operational problems during papermaking process.

Therefore, the solubility of precipitated starch in water at different temperatures was studied and the results are given in Figure 3. Figure 3 shows the solubility and swelling behavior of clay-starch composites as a function of temperature. The measurements indicated that the solubility of the composites below 70 °C was very low. However, the solubility was sharply increased at 70 °C, and almost 50% of starch composite was dissolved at 90 °C. The high solubility of the complex above 70 °C may relate to starch's gelation temperature.

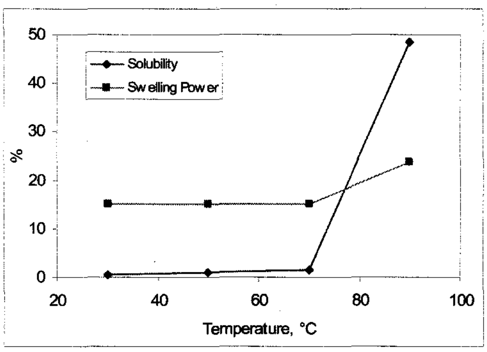


Fig. 3. Starch swelling power and solubility at different temperatures.

It is well known that starch molecules usually undergo a remarkable conformation charge at the gelation temperature. Because of this dramatic change, the bonding between starch and fatty acid molecules may be damaged or weakened so they are no longer able to be in the form of complexes. After determining the solubility at each point, the composites were centrifuged and freeze-dried to investigate the change of crystal structures. X-ray diffraction results indicated (not shown here) that the peak intensities for V-type inclusion complex (2θ=19.7°) and the fatty acid crystal (2θ=21.4° and 23.8°) decreased at the temperature above 70 °C. Another possible reason for the sharp increase in the starch-fatty acid solubility and decrease in crystalline peaks may be that the parts of the fatty acid combined with the starch can be leached out from the helical structure of starch over 70 °C and then the crystalline structures are disrupted. The volume change of coated starch was determined by swelling power. Previous reports *(16)* showed that the swelling power of starch-clay composites without fatty acids increased as the temperature increased. However, the swelling power of starch-fatty acid-clay composites did not change much at all conditions

studied. The low swelling ratio of starch-fatty acid complex relative to pure starch might be caused by the hydrophobicity of the fatty acids.

It has been known that the particle size and shape of filler have a direct relationship with the physical properties of paper (29, 30). Therefore, it is important to investigate the particle morphology for understanding the filled paper properties. Figure 4 shows SEM images of clay-starch composites.

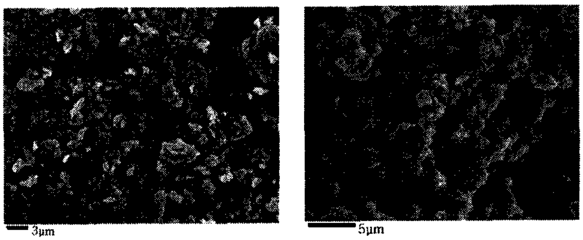


Fig. 4. SEM pictures of unmodified clay (left) and clay-starch composites by starch-palmitic acid complexation method (right).

It was found that the starch-fatty acid complex could perfectly coat the clay surface and form aggregates which are much bigger than pure clay. The aggregate size is not only the function of starch and fatty acid concentration, but also a function of the total solid concentration, stirring rate and time, ratio of starch to clay, pH, etc. For example, as shearing force or pH increased during composite formation, the size of composite aggregates decreased. It was found from the real time particle size measurement using FBRM that the mixture of clay with starch and fatty acid could not form aggregates effectively at pH 7 or values of higher.

The effects of clay-starch composites on paper strength and optical properties

Figure 5 shows the effects of clay-starch composites with two different palmitic acid ratios on paper physical properties. This result indicates that starch-fatty acid-clay composites could significantly improve paper strength properties compared to the pure clay. As the content of unmodified clay increased, the tensile strength of the handsheet made from unmodified clay decreased significantly because the clay particles in the handsheet interferes the fiber bonding, which reduces the number of inter-fiber bonds.

As shown in Figure 5, the tensile strengths of the handsheets made from two different clay-starch composites improved about 100~200% compared to the original clay at about 15% clay addition. As the palmitic acid content increased from 10% to 30% based on the starch solid weight, the tensile strength decreased. This result indicated that the increased hydrophobicity due to fatty acids interfered with hydrogen bond formation between starch and fibers.

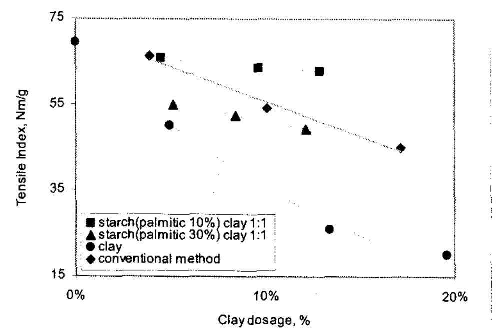


Fig. 5. Tensile strengths of the handsheet as a function of filler addition.

To compare the handsheets using clay-starch-fatty acid composites as filler with that using regular filler, the cooked cationic starch (0.1% solution) was used as a wet end additive for unmodified filler. To match the total starch amount in the composite, the same amount of cationic starch with the clay amount in the paper was added. For example, at 10% clay dosage, 10% of cationic starch based on total solid weight of the handsheet was added. It should be noted that this starch amount is much higher than the amount of cationic starch used in most papermaking processes. It is worth noting that when the cationic starch was added at 1~3 wt. %, large fiber flocs were formed. However, when the starch amount went up to 10 wt %, fibers were well redispersed and fiber flocs were not distinguished in the slurry, and the formation of these handsheets was very good. Although the fibers could be well dispersed with very high starch addition, the drainage rate was very slow. In real papermaking condition, this large amount of cationic starch can not be used because of price, slime or pitch problems, charge reversion, etc. The reason for using this high starch content in this study is to compare our approach with an extreme condition. Although the actual starch retention on the paper sheet was not measured, we believe it is much higher than the starch amount retained on paper sheet in a regular papermaking process. The result from this conventional wet-end addition method showed the tensile strength was much better than pure clay filler, but it had a lower tensile strength than the composite method (10% fatty acid). Because the starch was coated on the filler surface in our approach, both the starch retention and water drainage were very high for our approach. Therefore, one of the significant advantages of this starch-clay composite approach is that very high starch content can be used for paper physical property improvement without starch retention problems.

Figure 6 shows the results of z-direction tensile strengths of clay-starch composite filled sheets. It is well known that the ZDT usually decreases as the filler content in the paper sheet is increased because filler interferes the fiber-fiber bonding.

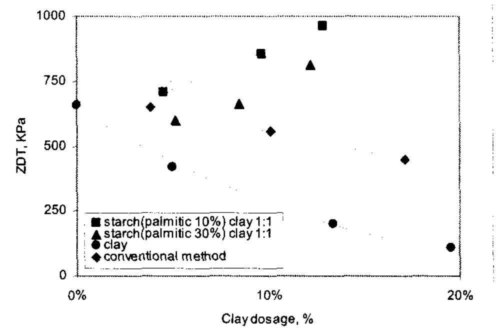


Fig. 6. Effect of clay-starch composite on ZDT strength of the handsheets.

However, surprisingly, the ZDT increased as the composite content increased in the handsheets made from clay -starch composites with a ratio of clay to starch of 1:1. The result from the conventional wet-end method using cationic starch showed that as the clay amount increased, the ZDT decreased. Other physical properties such as burst and folding strength were also significantly improved about 200~300 % (not shown here). The main reason for this significant improvement is believed to be an increase in bonding strength between wood fiber and clay-starch composite filler as shown in ZDT test. Figure 7 shows the brightness of the handsheets made with pure clay and clay-starch composites.

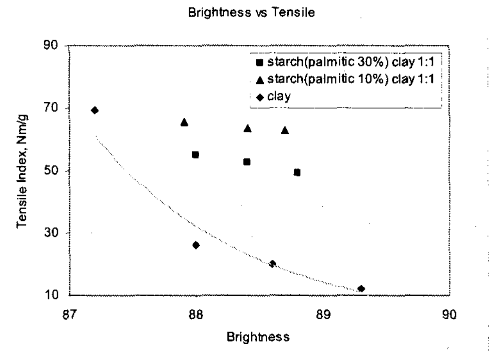
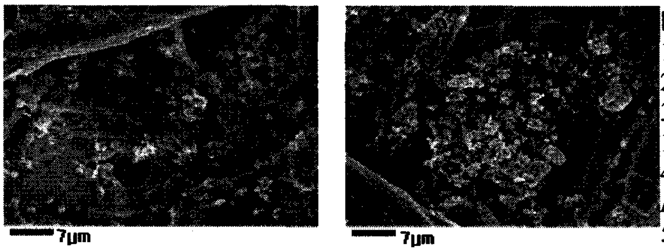


Fig. 7. Effect of clay-starch composites on brightness of the handsheets

Clearly, at the same tensile strength, the brightness of handsheets filled with the clay-starch composite was much higher than that of pure clay because much higher filler content was in the handsheet made from composite. It results suggests that, at the same paper tensile strength, the brightness of the paper can be improved by using starch-fatty acid-clay composites.

In order to investigate the bonding between the wood fibers and composites and uniformly distribute composites on the paper, the surface of the handsheets filled with composites was observed by SEM as shown in Figure 8.

All clay-starch composites were stuck on the wood fiber surface and no individual clay particles were observed. The SEM picture also clearly showed that the thin starch film was spread over both filler particles and fibers. Obviously, this starch film will enhance the bonding strength of the handsheet. It is believed that the starch-film was formed during drying at 105°C.



8. SEM pictures of clay-starch composite filled handsheets. (left: palmitic acid 10% to starch, right: palmitic acid 30% to starch)

It is also shown that the clay-starch composites with 10% fatty acid addition were distributed uniformly on the handsheets compared to the clay-starch composites with 30% fatty acid. This agrees well with the brightness results, i.e. the handsheets made from clay-starch composites with 10% fatty acid have higher brightness values than those with 30% fatty acid.

One of the additional advantages of using clay-starch composites formed by fatty acid is that the fatty acid in the composites can increase the hydrophobicity of the filler, so the water repellent property of the paper sheets increases. The images from contact angle measurements showed that a much higher contact angle of water on the handsheets could be obtained even after 60s. However, a water droplet was immediately adsorbed into the handsheet with pure clay. It was also found that as the fatty acid ratio increased and the composite dosage increased, the wettability of the handsheets decreased. Even though the sizing degree of the composite filled paper may not be as high as AKD or ASA sized papers, the improvement in the hydrophobicity of paper sheets using starch-fatty acid-clay composite will significantly reduce the dosage of sizing agent during papermaking.

CONCULUSIONS

This study provided a method of clay-starch composite preparation by starch-fatty acid complexation. Thus, the composite prepared can be used as a papermaking filler with much higher paper strength than untreated clay. From the physical property measurements, clay-starch composites could increase bonding strength dramatically as shown in ZDT tests, thereby the tensile strength was improved up to more than 100~200% at 15% composite addition compared to untreated clay. The optical properties increased as the composite amount in sheets increased.

At the same brightness, the clay-starch composite filled handsheets have much higher tensile strength than unmodified clay filled sheets. Additionally, handsheets filled with clay-starch composites improved the water-repellant property due to the hydrophobicity of the fatty acids. The bonding of clay-starch composites with fibers was confirmed by SEM. The starch-fatty acid complex method reported in this study has many advantages for paper grades that need high filler loading, high physical strength with certain sizing requirements.

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