

Development of adhesives from Rice & Cassava Starch

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ABSTRACT

Potentials of corrugating adhesive production from cassava and Rice starch varieties were investigated. Rice variety used was BG 358 and the cassava varieties were identified as *Manihot utilisima*. Corrugating adhesives produced were compared with a commercial adhesive sample which was made of corn starch along with modified corn starch. Based on the results obtained formulations were developed for optimal process conditions for each type of starch. This yielded products comparable to that of the industrial sample. Products obtained from these new formulations were found to have relatively improved bond strength in terms of tensile values and has the same viscosity as the reference sample. These starch dispersions were found to be shear thinning liquids, hence had to avoid the usage of common viscometers. Viscosities were measured in terms of Efflux Seconds by a viscosity cup called Ford cup with an orifice diameter of 4mm. Tapioca starch based corrugating adhesive developed was found to possess higher tensile values and higher yield than that of the rice starch based corrugating adhesive that was developed. Overall the type of carrier starch was found to affect the rheological characteristics of the corrugating adhesive.

INTRODUCTION

Starch as the prime reserve polysaccharide in plants is arranged in linear or branched configurations namely amylose and amylopectin. (International Starch Institute)

Basically the chemical properties of starch are based on this structure. Starches act as pseudo thermoplastic materials and due to this reason they are not readily soluble in water. Collectively hydrolysis (alkaline/acid) and gelatinization of starch particles would add an adhesion character into this pseudo plastic emulsion. (Olagoke Olabisi, 1997) Rheological behavior of such dispersion depends on several parameters. Raw starch is the main component in several commercial products such as a wide range of adhesives, foods, laundry starches etc. However most of them need starch to be hydrolyzed or cleaved into fragments. This process results in giving characteristic properties that could differentiate one commercial product from another. Depending on the solid content, an adhesive could be categorized as "low/high" solid adhesives. Mostly corrugating machines with higher runner speeds would prefer high solid type. (Bozich, Jr., Frank A, 1990)

Starch is present in granules which can be broken down, imparting various physical and chemical properties in the final product as mentioned earlier. Its capability of gelatinizing would account for various changes in physical properties. Gelatinization is when the water portion in a starch slurry which contains starch granules, prevail over hydrogen bonding within the granule resulting a distinct swelling. (Bhuvnesh Goswami, Rajesh D. Anandjiwala, David M. Hall, 2004) This happens at a specific temperature named as “gelatinization temperature’ and it is a characteristic value for each starch type. Normally the gelatinization temperature is about 60-64 °C. When the temperature rises, the amount of swollen granules in the slurry rises. This leads to an amplified viscosity in the system. Likewise the size of the swollen granule rises accordingly. They acquire a state of fragility owing to their swollen structure. This has a propensity of fragmentation when the shear built inside the container rises. A resultant decline in the viscosity will be noticed consequently. Collectively these two opposing properties would result in an increase in viscosity when gelatinization becomes predominant over fragmentation. When fragmentation equals gelatinization viscosity would have reached a peak value. Again it declines when fragmentation major over the swelling effect and reaches a stabilization point when both these effects are insignificant. (Black, William C., 1977)

Progression of gelatinization is compiled of numerous stages. Such a system is in a non-equilibrium state. The rate of gelatinization could vary on the factors like hydrolysis which could directly affect gelatinization by facilitating its mechanism. Hence when all other environmental variables are maintained constant and only the degree of hydrolysis is varied it indirectly signifies the degree of gelatinization.

Powerful alkali states would compel starch to gelatinize even at room temperature. This observable fact is frequently used in the production of adhesive pastes. Gelatinization is of two types; thermal and chemical (alkaline). Evaluation of thermal gelatinization against the later discloses important facts which could definitely count for the feasibility of chemical gelatinization over thermal. (H. Yamamoto E. Makita, Y. Oki and M. Otani, 2004)

Particle size of starch granules could vary if an assortment of starch types is taken in to consideration. From the data obtained the particle size of cassava starch is of smaller diameter than of rice starch. In Rice it has been recorded that most of the starch granules are from 2 to most often 6 microns, seldom up to 10 microns with many agglomerates. Only these agglomerates would possess spherical shapes while the rest will be of irregular shapes. But in cassava most of the granules are of smoother spherical shapes than of rice starch. These could also account for different rheological properties of starch dispersions. (International Starch Institute)

Corrugating adhesives can be prepared via various pathways. But the most preferred method is the “Stein-Hall” type. That composed of two parts. Chemically cooked/career starch portion and the uncooked/raw starch portion are the two distinct parts that the user should mix at the time of usage. Career starch is set up by mixing a desired amount of starch

in adequate amount of water followed by the addition of caustic soda. The mixer is then agitated thoroughly. Raw starch is a dispersion of starch and a minute amount of borax or boric acid in water which results in a borating complex is the resultant. In the preparation of the adhesive chemically cooked starch is added to the raw starch slurry followed by moderate stirring. Corrugating adhesive containing a solid percentage of about 17 to 25 by weight or a viscosity of about 150 to 250 cp, can be produced in this way. In general, the film applied over the corrugating paper board is about 10-14g/m². Starch based adhesives are usually not moisture resistant. If a degree of moisture resistance is needed for any corrugated box type, the starch used at the beginning has to be modified or a polymeric material should be added to obtain such qualities. Hence the end product would be of a higher cost. (Vandavelde and Daniel, 2006)

When the adhesive film is applied on the fluted tips of the corrugated paper, the carrier starch portion wets and penetrates the medium and liner to form a bond. Hence this wetting and penetration are of a great importance in forming the adhesive joint. During the application of heat, the temperature in the bonding zone is increased gradually above the gel point of the slurry starch. However in this study heat was not applied and the paper strips were kept under normal environmental conditions during the entire curing period. Raw starch granules begin to enter the solution by drawing water from the carrier starch. The carrier starch begins to fasten (setback) to the paper fibers as it loses water. When the slurry starch gels, it becomes more viscous and further penetration into the paper becomes difficult. Set back occurs within the adhesive that leads to fiber bonding. Water removal dries the paper that cures the bond. (Royal Institute of Technology Sweden) Important variables for the applying and distributing the adhesive on the substrate are the surface contact angle, adhesive viscosity and the chemical resistance of the substrate to the adhesive. (DSM Engineering plastics article, 2008)

Keeping the above concept as the base for this adhesive bond formation one could choose a mechanism similar to the mechanical interlocking theory to depict this phenomenon. According to this theory it is completely a physical interaction that is needed. A microscopic view of the surface of a paper shows a very rough exterior exhibiting crevices, cracks and pores. The adhesive applied gets penetrated into these features and hardens such that it “keys” into the surfaces analogue to “locks” and forms a strong surface bond. The adhesive thus is able to bond two surfaces together. Therefore the main criteria for achieving a good adhesive bonding are surface wetting and penetration of the adhesive during the curing time.

For a corrugating adhesive to be effective it should possess few characteristics such as, high bond strength, tack development, viscosity stability, cost effectiveness, low energy consumption, extended pot life, increased moisture resistance etc. (Leake Craig, Atkinson Jeffrey G., Foran Michael, 1992) Viscosity stability plays a critical role among these since it is a compulsory requirement for a constant and a uniform glue pick up and for a better

runnability of the corrugators. Thereby if the adhesive applied is too much or too less, warp or loose liner and delamination could be the resultant. (Harper/Love Adhesives Co-operation, 2007)

MATERIALS AND METHODS

Rice flour Preparation

A mutant strain of white raw rice (BG 358) was selected in this study as the source of rice starch. Paddy sample obtained from the Agricultural Department, Hambanthota, Sri Lanka was milled and raw rice obtained. Milled rice was soaked in water for 12 hours prior to grinding. Rice grains were ground using the grinder (Japan model no; IS-4250) RPM 14000/18000 for 1hour (Operational 5 minutes on and 3 minutes off). Half the amount of the ground rice flour was sieved using a sieve with 250 μm and a diameter of 21 cm using the shaker (model No-EFLIMT, 50 Hz) for two hours.

Rest was found to be in the range of 250- 355 μm in particle size. Two flour samples were obtained with two difficult particle sizes likewise. Both the samples were stored in the refrigerator under 40-37°F until the analysis is done.

Cassava flour Preparation

Debarked roots were washed peeled and sliced in to (2cm) strips. Tray dried under natural atmosphere for about one day. Sun dried cassava strips were ground using a grinder (Japan model No IS 4250) RPM 14000/18000 for 1hr.(Operational 5 minutes on and 3 minutes off) Half the amount of cassava flour was sieved using a sieve with 250 μm and a diameter of 21 cm using the shaker (model No-EFLIMT, 50 Hz) for two hours.

Rest was found to be in the range of 250- 355 μm in particle size. Two flour samples obtained with two difficult particle sizes likewise. Both the samples were stored in the refrigerator under 40-37°F until the analysis is done.

Adhesive Preparation

The carrier component is prepared by chemically cooking 5g of starch in 34.42g of water. A total of 1g NaOH is dissolved in 3g of water. Alkali solution was then added to the starch slurry. It was agitated for 10 minutes. 10g of water was then added in order to cool the system and quench the reaction.

Raw portion was prepared in a separate vessel. 31.5g of starch was added to 132.55g of water followed by the addition of 0.6g Borax (Pentahydrate). After 5 minutes of moderate agitation the carrier starch was slowly added to the raw starch slurry and moderate

agitation was continued. This resulted in an adhesive having a total starch solid content of 18%-21%

Effect of increased NaOH concentration on adhesive behavior was assessed by preparing 5 samples designated as A, B, C, D, and E by following the same procedure as mentioned above. Only the NaOH concentration was varied. Alkali solution series prepared were of (w/w) 20% 26% 33% 40% 46% (For rough tuning) and 40% 41.6% 43.3% 45% 46.6% (For fine tuning)

Adhesive samples obtained using cassava starch via the above mentioned formulation were found to be too viscous. Hence an additional water content of 40ml was added to adjust the viscosity of such samples to bring back to our study range.

Testing the effect of carrier starch

Same formulation was carried out with 43.3% of NaOH. 5g of starch in the carrier portion was proportionally divided as 4:1, 3:2, 2:3 and 1:4 (rice: cassava). Due to high viscosity obtained beyond our study range, only 4:1(rice: cassava) proportion was selected as the most suitable sample mix where its viscosity and adhesiveness is concerned.

Tensile Test

Ultra Test tensile machine/ advanced force Gauge, Mecmesin Ltd with a capacity of 100N was used. Craft paper used for the test was 140 KTAL. 1.5cm width and 7cm long strips were used in the study.

Thin, uniform adhesive film was applied on the paper strips with the help of a cotton bud. Strips were kept undisturbed under constant pressure during the curing period of 6 days. After the curing time is completed the tensile values were taken from the tensile test machine and the tensile values obtained were recorded.

Viscosity measurements

Ford cup viscometer No.04 with an orifice diameter of 4mm was used. With the stop watch ready and a finger over the orifice, sample was poured into the cup and when the finger is taken, switches on the stop watch at the same time. The time it takes for the liquid to flow through the orifice until the first break in the liquid stream was recorded.

Keeping quality analysis

Viscosity stability was measured by taking 3 samples in to consideration those were prepared according to the same formulation but with different water content to adjust the initial viscosity.

Rice, cassava and rice-cassava mixed samples were taken in to consideration. Viscosity measurements were taken after each consecutive hour and were recorded.

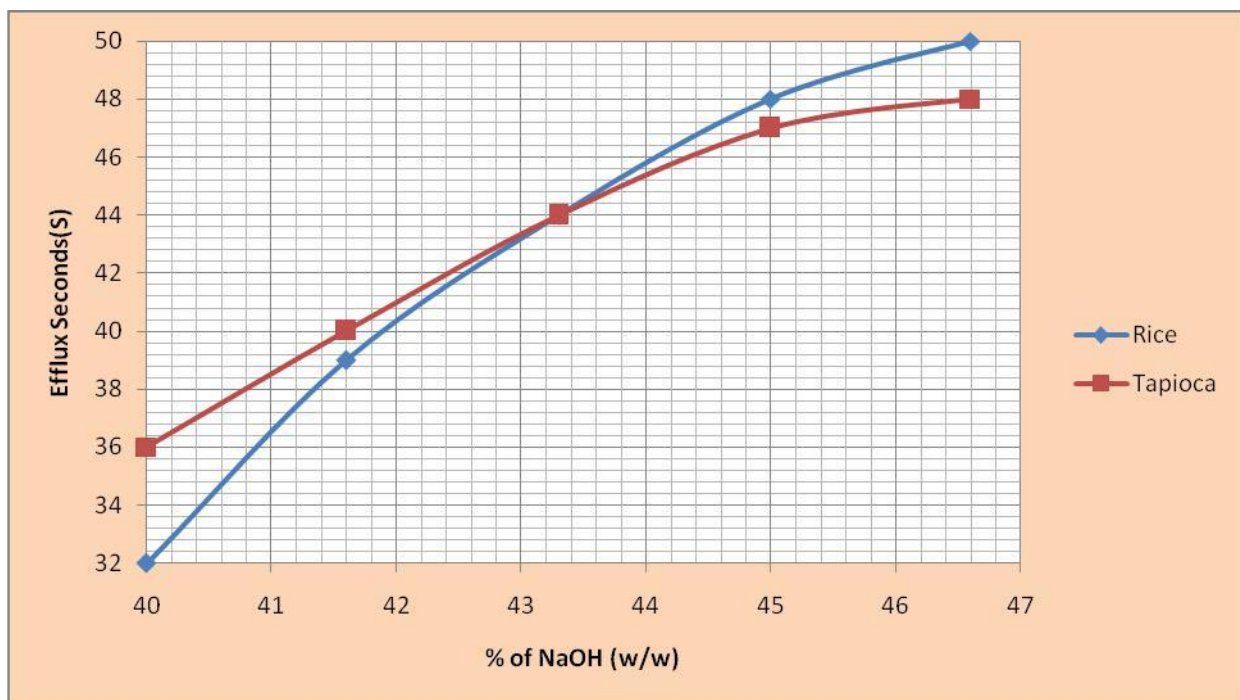
RESULTS AND DISCUSSION

The results of the experiments carried out are presented in table No. 01, 02 and 03. The plots of each data series is accordingly Graph No. 01, 02 and 03.

Table No: 01

| % of NaOH (w/w) | Rice(Efflux seconds) | Tapioca(Efflux seconds) |
|-----------------|----------------------|-------------------------|
| 40 | 32 | 36 |
| 41.6 | 39 | 40 |
| 43.3 | 44 | 44 |
| 45 | 48 | 47 |
| 46.6 | 50 | 48 |

Graph No. 01



When different NaOH concentrations were plotted against the viscosity of the adhesive sample produced, curves obtained show an increase in the viscosity when the % of NaOH in the carrier portion was increased. However the curves possess a prominent gradual decrease in gradient. These can be discussed in terms of few effects as stated below in the discussion.

Along with the increase in alkali concentration, the degree of alkaline hydrolysis increases. This results a rise in viscosity of the system. Meanwhile fragmentation takes place as well. They have contradictory effects on the system's viscosity. However the collective accommodation of an increase in viscosity could provide evidence that the degree of fragmentation at this point could have been suppressed by the higher degree of hydrolysis. It has facilitated gelatinization indirectly.

In addition to that, the ionic strength of the system increases accordingly when the alkali concentration has gradually risen. This also could be another factor which improves the solvent quality facilitating a higher degree of hydrolysis in both the curves.

Apart from that, few other factors such as the filler particle size and shape also could account for this amplification of viscosity.

When the average particle size declines the strength embedded in these fillers decreases. Therefore the hydrolytic effect is enhanced to a considerably greater extent resulting a higher degree of gelatinization.

The shape of the filler particle can facilitate the degree of hydration by providing greater spacial vicinity. If same volume fractions of rice and cassava starch samples are considered, cassava starch would contain comparatively more number of starch granules owing to its high order of arrangement. Due to this reason a higher degree of gelatinization could be expected in cassava starch. Hence the adhesive preparations done using cassava starch through the same formula demonstrated a very high viscosity. To bring it down to a desirable level which is in the range of this study, extra content of water (40ml) has to be added diluting the sample.

Explaining the prominent decrease in gradient of both the curves, one could come up with a hypothesis as developed below.

Several inclusion complexes could also suppress the gelatinization and hydrolysis at the same time. These complexes can be believed to be stable at the initial stages of low NaOH concentrations. Since this study was conducted at room temperature, instabilization of these complexes via a thermal pathway also had been avoided indirectly.

Amylose-lipid complex which could be formed usually dwell in the ungelatinized starch fraction disturbing the progress of gelatinization. NaOH infiltration into such a complex could form sodium salts of superior fatty acids when encountering the lipid portion of it. This effect further could disturb gelatinization to a considerable extent due to the formation of powerful complexes. Having large hydrophobic and hydrophilic groups these complexes might possess strong surfactant character. Polarity has a significant role to be played here. This in fact could stand for the modification of texture as well as viscosity in adhesive samples with different degrees of gelatinization. Polar surfactants/emulsifiers which could have formed likewise with amylose might have a chance to confine the swelling and the degree of solubility of the ungelatinized starch fraction.

Also there can be a charge screening in such a system of adhesive. Interactions between charges which are needed in hydrolysis can get reduced in strength or screened by the presence of many nearby water molecules, ions, and other starch fragments which can be partially charged at the moment. This would result a little 'counterion cloud' which neutralizes its charge, and therefore the degree of hydrolysis could get slowed down.

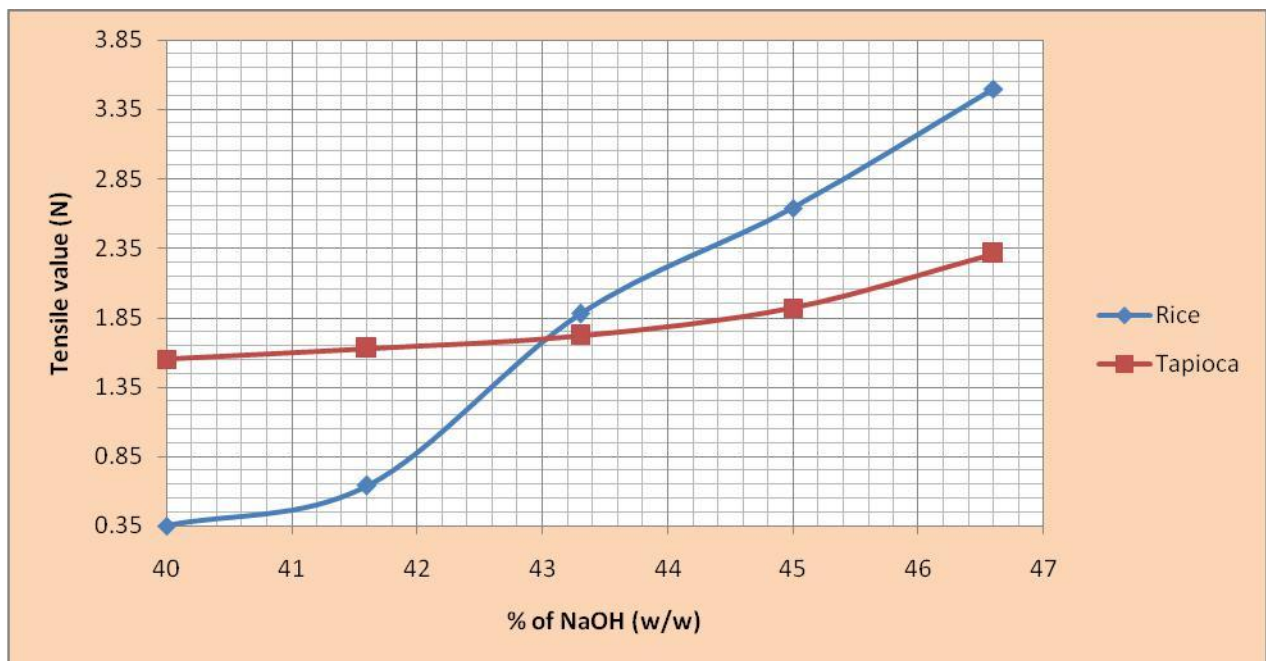
Partially hydrolyzed starch chains with partial charges would provide the most significant positive effect towards this phenomenon. (S. A. Roberts and R. E. Cameron, 2001)

Collectively these effects would decrease the degree of swelling momentum of starch granules throughout the initial stage. Further research is needed for clarification of these suggestions in terms of kinetic studies.

Table No.02

| % of NaOH (w/w) | Rice-Tensile value(N) | Tapioca- Tensile value(N) |
|-----------------|-----------------------|---------------------------|
| 40 | 0.35 | 1.55 |
| 41.6 | 0.64 | 1.63 |
| 43.3 | 1.88 | 1.72 |
| 45 | 2.64 | 1.92 |
| 46.6 | 3.5 | 2.31 |

Graph No.02



When plotting the alkali concentration against the tensile values obtained, prominent increase in both the curves have been detected. There is a clear deviation between the two curves. Tensile values obtained from tapioca starch based adhesive shows better performance than rice starch based adhesive in the beginning, but fails to retain it at the end. After a certain concentration of NaOH added, rice starch seems to perform better.

For both the types of samples tensile values increased with the increase of concentration of alkali added in the carrier portion. During hydrolysis a long starch polymer molecule breaks

in to short structures. Owing to the degree of this short structure resulted viscosity of that particular system would vary.

Molecular inter diffusion can be facilitated by such short structures; therefore it is easier to achieve good adhesion upon such conditions. (Tate & Lyle Amylum Group) In addition to that these short structures of starch molecules could accelerate the process of gelatinization also. Collectively a sturdy tack development could be expected. In such systems when the glue is positioned only on the flute tip, exactly where it is supposed to be to guarantee a strong bonding, resulting less significant splashing; consequently, lower glue consumption is needed, resulting in lower moisture input, higher speeds and improved board quality thereafter.

Better tensile values obtained from cassava starch adhesive samples could be supported by few chemical and physical characteristics of cassava starch. From the data obtained, cassava is found to contain 1-2% of fiber and in rice it is normally lesser than 0.2%. (International Starch Institute) These fiber strands could enhance the “holding” character of its starch/filler particles, effectively in increasing its adhesiveness. (Wallace and Jack R, 1998)

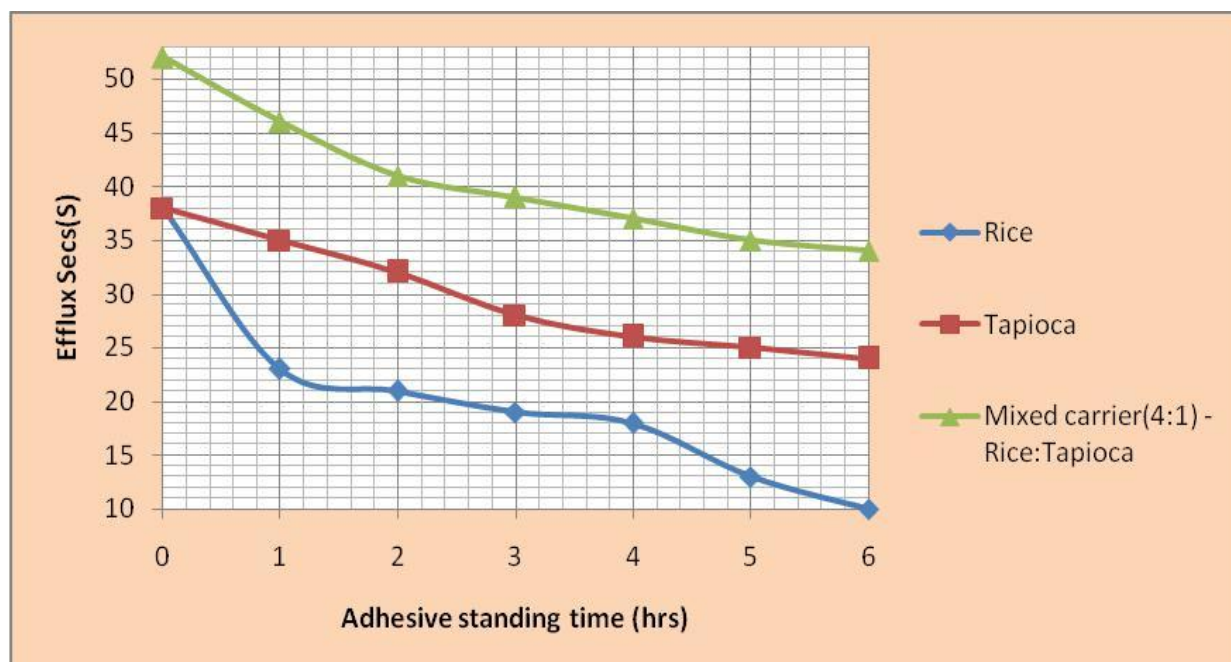
However after a certain point the values obtained from rice starch based adhesive is known to possess better qualities than that of tapioca starch based adhesive developed.

This could be owing to the fact that when the carrier starch is good, subsequently bond strength, setting speed, good tack development, and improved runnability could be achieved. (Fang Zhong, Yue Li, Ana Marie Ibanz, Moon Hun Oh, Kent S. McKenzie and Charles Shoemaker, 2008),(Eden James, Kasica James, Leake Craig, Lacourse Norman, Altieri Paul, 1996) Hence when considering the amylose content in rice and tapioca starch portions, rice starch with lesser moisture content would possess higher starch percentage and subsequently, an elevated amylose fraction as well. Taking this in to consideration rice should possess higher adhesiveness. But it could be retarded to a certain extent due to higher protein and lipid content present when compared with cassava starch, as explained earlier.

Table No. 03

| Adhesive standing time (hrs) | Rice-Efflux seconds | Tapioca-Efflux seconds | Mixed carrier(R:T) 4:1-Efflux seconds |
|------------------------------|---------------------|------------------------|---------------------------------------|
| Initial | 38 | 38 | 52 |
| 1 | 23 | 35 | 46 |
| 2 | 21 | 32 | 41 |
| 3 | 19 | 28 | 39 |
| 4 | 18 | 26 | 37 |
| 5 | 13 | 25 | 35 |
| 6 | 10 | 24 | 34 |

Graph No.03



Curves obtained after plotting the values obtained by keeping these three samples for few hours without external disturbance, show an outstanding decrease with various gradients. Out of them, the adhesive sample made out of rice starch shows a sharp decrease where in the tapioca starch based adhesive has a gradual decrease.

However when carrier starch is made out of 1: 4, tapioca: rice starch along with the same alkali concentration shows a comparatively better keeping quality than that of rice starch based adhesive.

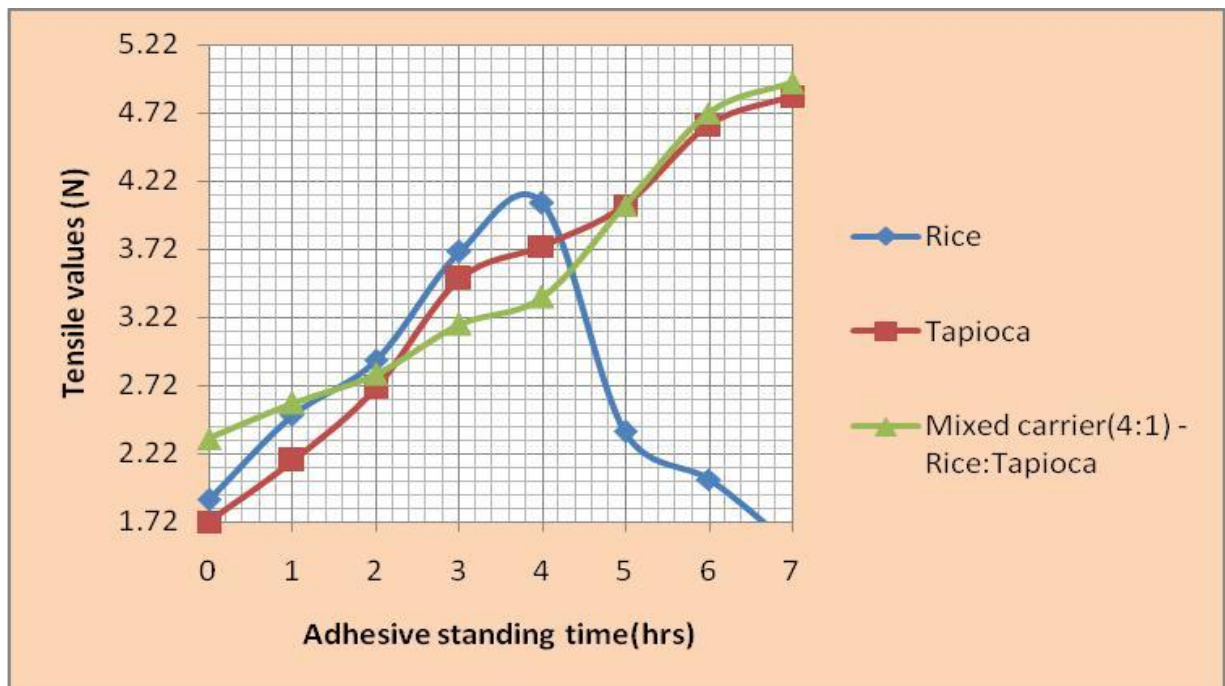
These curves could be the resultant of non-Newtonian behavior of the adhesive dispersions made. They possess shear thinning character and as a result the viscosity of the system becomes entirely dependent on time and it decreases at different rates.

Apart from the above mentioned physical behavior of the dispersion, few other factors too contribute to this effect. Such as the added NaOH may possibly bring a chemical instability which could affect the previously mentioned amylose-lipid inclusion complexes. As it is a well proven fact that amylose is proficient in arresting various chemical composites together with alkali hydroxides such as NaOH and to build novel types of complexes. These novel complexes would normally have an effect on the gelatinization behavior resulting radical transformations in viscosity with time. (H. Yamamoto E. Makita, Y. Oki and M. Otani, 2004)

Table No. 04

| Adhesive standing time (hrs) | Rice-Tensile values(N) | Tapioca- Tensile values(N) | Mixed carrier(R:T) 4:1- Tensile values(N) |
|------------------------------|------------------------|----------------------------|---|
| Initial | 1.88 | 1.72 | 2.33 |
| 1 | 2.5 | 2.17 | 2.59 |
| 2 | 2.9 | 2.7 | 2.8 |
| 3 | 3.7 | 3.5 | 3.17 |
| 4 | 4.06 | 3.74 | 3.37 |
| 5 | 2.38 | 4.04 | 4.04 |
| 6 | 2.03 | 4.63 | 4.72 |

Graph No. 04



Plotted curves show tensile values against time as shown. All the three curves show an increase in tensile values with time initially. But rice starch based adhesive paste could not retain such character after a certain point and thereafter tend to lose its tensile value sharply.

According to steps of the bonding mechanism the degree of wetting and penetration plays major roles in forming a strong bond. The decrease in viscosity has facilitated the above mentioned phenomena. But in the case of rice the thinning character of rice starch based adhesive could be too thin as to hold the adherent to the adhesive paste.

CONCLUSION

In this study basically the flow property of the dispersion of rice starch as well as tapioca starch was investigated. Which would stand for seed originated starches and tuber starches. Therefore the alkaline concentration dependence of the flow performance was well studied. The time dependence of viscosity was observed for a certain alkali concentration effecting the alkali gelatinization of rice starch and tapioca starch.

In this study the fundamental objective of investigating a formulation for a better corrugating adhesive which is comparable to the industrial sample was achieved. This would assist in obtaining adhesives with better performance by using locally available raw materials in order to cut down the importing costs, on which this entire field is currently dependent on.

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