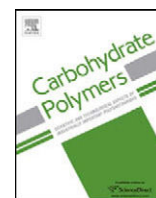




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Carbohydrate Polymers

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Improving wet and dry strength properties of recycled old corrugated carton (OCC) pulp using various polymers



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ARTICLE INFO

Article history:

Received 20 October 2012

Received in revised form 2 January 2013

Accepted 13 January 2013

Available online 4 February 2013

Keywords:

Chitosan

Cationic starch

Wet-strength

Old corrugated carton

Poly (vinyl alcohol)

ABSTRACT

In this study, the application of different dosages of low and high molecular weights (MW) of chitosan (Ch), cationic starch (CS) and poly vinyl alcohol (PVA) were systematically investigated using old corrugated carton (OCC) furnishes. Various sequences of above-mentioned polymeric additives were also examined to find out the optimal combination for improving both wet and dry tensile strength. For each treatment, 4 handsheets, each having basis weight of 100 g/m², were made. In general, the tensile strength of handsheets was significantly affected by the addition of polymeric agents. The enhancing effect of additives on dry tensile property was much higher than wet condition. The results also showed that the tensile strength of the samples made from OCC furnishes were improved upon the addition of high molecular weight chitosan (ChI) compared to the untreated ones (control). The low MW chitosan did not change the properties of handsheets dramatically. Application of polymeric agents moderately decreased the stretch to rupture, however with increasing dosage the stretch was improved. Sequential addition of used polymers showed that triple application of polymers was beneficial to both dry and wet tensile strength, although the effect was larger for dry. The best results in wet and dry tensile strengths were achieved using sequential of PVA–ChI–CS. Sequential addition of oppositely charged polymers forms a macromolecular layered structure of polyelectrolytes.

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1. Introduction

In recent years, the availability of wood-based pulps has been of great concern. Extensive research has focused on exploring a suitable substitute for conventional forest based materials used in papermaking manufactures (Fatehi, Tutus, & Xiao, 2009). Among the possible alternatives, the development of pulp and paper using recycled paper is currently at the center of attention (Ghasemian, Ghaffari, & Ashori, 2012). Today, the application of waste paper is steadily increasing in the world, due to the environmental concerns, population growth and the shortage of wood supply. Old corrugated carton (OCC) paper is the most significant category of waste papers for recycling, based on the percentage of recovery rate and by tonnage (Ashori & Nourbakhsh, 2008). However, by increasing the number of cycles in the fiber recycling, the strength of papers is gradually reduced, which is mainly due to the decrease in the fiber bonding strength through the hornification phenomenon (Hamzeh, Najafi, Hubbe, Salehi, & Firouzabadi, 2012). It has been claimed that the strength of such recycled fibers is not sufficient to meet the industry's demand; thus, the strength should be improved.

One approach to improve the strength of recycled fibers is to use dry strength additives. They are usually water soluble, hydrophilic, natural or synthetic polymers. The most common chemicals used commercially are cationic starch (CS) and polyvinyl alcohol (PVA). Dry-strength polymers can interact with fibers in a number of ways. In order of increasing bond strength, these interactions are generally termed as van der Waals forces, hydrogen bonding, ionic attractions and covalent bond formation. The majority of paper strength additives function on the first two of these energy levels, relying primarily on multiple hydrogen bond formation for their retention and effectiveness. Starch, for example, which has sufficient molecular size to span inter-fiber distances and also has a proclivity for forming hydrogen bonds with cellulosic materials, clearly functions by increasing the number of low energy bonds between fibers. In order to gain good retention and improve the efficiency of starch utilization on papermaking fibers, cationic starch was developed (Malton, Kuys, Parker, & Vanderhoek, 1997), which promotes strong adsorption onto fibers, fines and fillers through electrostatic attraction to the anionic groups on the surface of the fibers and particles. Controlled penetration, high binding strength, and reduced effluent loads are important benefits that are often derived from the use of cationic starch (Glittenberg & Becker, 1998).

Poly (vinyl alcohol) (PVA), which is one of the most dominant polymers, has several applications in papermaking processes. PVA

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is widely recognized as one of the strongest binders available in the paper industry, and depending on its molecular weight, can be 3–4 times stronger than starch (Fatehi et al., 2009). Due to the presence of hydroxyl groups in every repeating unit of PVA, it appears to be one of the best polymers to reinforce cellulose fibers (Pelton, 2004). In addition, it has excellent film forming potential (Lertsutthiwong, Nazhad, Chandkrachang, & Stevens, 2004). PVA can tie down the fines and help bind filler particles to the fiber, both of which are advantageous in printing papers. In papermaking, PVA is used for surface sizing to form films with very high tensile strength and high degree of transparency, flexibility and oil resistance (Briscoe & Luckham, 2000). PVA can also be mixed with starch and applied at a size press (Zakrajšek, 2008).

In papermaking, chitosan has been found to be effective as dry and wet strength agent (Laleg & Pikulik Ivan, 1991; Lertsutthiwong, Chandkrachang, Nazhad, & Stevens, 2002; Ashori, Jalaluddin, Wan, Zin, & Mohd Nor, 2006) as well as in coating (Kjellgren, Gällstedt, Engström, & Järnström, 2006), sizing (Laleg & Pikulik Ivan, 1992; Lertsutthiwong et al., 2004; Ashori, Raverty, Vanderhoek, & Ward, 2008), and retention (Li, Du, & Xu, 2004a). Chitosan, a biodegradable, nontoxic, antibacterial, as well as renewable resource, is the second most widespread natural polysaccharide (Li, Du, Xu, Zhan, & Kennedy, 2004b). It is the acid-soluble deacetylated derivative of chitin, prepared by reacting chitin with an aqueous hydroxide solution (Fig. 1a and b). Chitin and chitosan belong to a very interesting family of β -(1–4) linked polysaccharides. This kind of glycosidic linkage leads to relatively extended and rigid structures in the solid stage, particularly in the dry state (Kumar & Majet, 2000). The primary structure of chitosan is similar to cellulose except that the C-2-hydroxyl group of cellulose is replaced by an amino group (Laleg & Pikulik Ivan, 1993). Chitosan is insoluble in water under alkaline conditions, but because of its primary amino groups it is soluble in acidified water (Fig. 1c).

The first and important goal of the paper production is to make a product with the customer demanded quality specifications as economically as possible. This requires a good runability of paper machine that is often evaluated by the number of web breaks in proportion to production speed. Most frequently, the paper web breaks occur after couch roll when weak wet web is transferred unsupported between two machine parts in a so-called “open draw”. Wet web strength can be developed by increasing the fine and long fiber proportion in furnish, pulp refining, and solid content of sheet (Ferreira & Guimarães, 2003). Despite the significant effect of wet-web strength of runability of paper machine, in the past very few attempts have been made to increase the wet-web strength (WWS) of paper by chemical additives (Laleg & Pikulik Ivan, 1991, 1992). The improvement of wet paper web strength, and consequently enhancing paper machine runability through the various chemical additives, has received a great attention in recent years both from academics and papermakers (Tejado, Miro, & van de Ven, 2011; Kataja-aho, Haavisto, Asikainen, Hyvärinen, & Vuoti, 2011).

In this work, different dosages of chitosan, PVA, and cationic starch were individually added to the OCC furnish and the hand-sheet properties in terms of dry and wet tensile and stretch properties were investigated. In addition, various sequences of combination of polymeric additives were examined to find the optimal combination for improving both wet and dry strength.

2. Materials and methods

2.1. Materials

The lignocellulosic material used for this study was OCC recycled paper which was obtained from local recycling paper mill. The OCC paper was cleaned and dispersed in the disintegrator, after which it was fluffed and refrigerated until use.

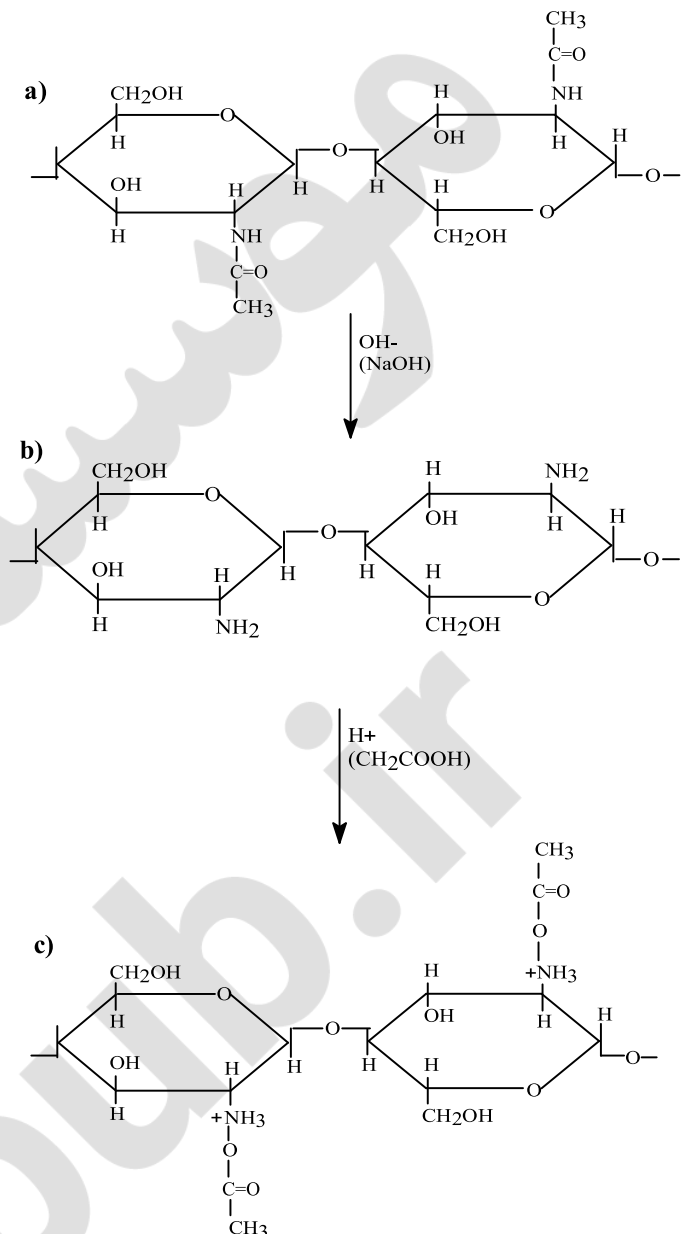


Fig. 1. Chemical formulas of chitin (a), chitosan (b), and chitosan acetate form (c).

Four additives used in this study were: chitosan (Ch) with two different (low and high) molecular weights, cationic starch (CS) and PVA. The characteristics of used polymers are presented in Table 1. All stock solutions were freshly prepared to avoid any possible degradation.

2.2. Application of polymers

In this work, the chitosan solution was prepared by dissolving chitosan in aqueous 1% (w/w) acetic acid at room temperature by stirring for 8 h, whereas the PVA was prepared by dissolving PVA powder in distilled water and heating on a hot plate with a magnetic stirrer at 70–75 °C for 20–25 min. The cationic starch was prepared by suspending starch powder in distilled water and heating to 95 °C on a water bath with periodic stirring, and then holding the suspension at this temperature for 25–30 min after the onset of gelatinization. The solutions were then diluted with distilled water, and refrigerated prior to use.

Table 1
Characteristics of the used polymeric materials.

Parameter	Ch I	Ch II	CS	PVA
Source	Shrimp shell	Shrimp shell	Potato	–
pH	–	–	7.0	5.5–6.5
Viscosity, cP	250	200	40	68
Solubility, %	99.9	99.9	100	100
Ash content, %	0.45	0.45	0.30	–
Moisture content, %	7.5	8.0	14.0	11.6
Molecular weight, Da	9×10^5	0.6×10^5	–	1.3×10^5
Degree of deacetylation, %	>75	75–85	–	–
Supplier	Sigma–Aldrich	Sigma–Aldrich	Lyckeby Amylex	Sigma–Aldrich

Chitosan was applied in dosages of 0.25%, 0.5%, 0.75% and 1.0%, while cationic starch was used in dosage of 0.5%, 1%, 1.5% and 2% based on oven dried weight of the pulp. In addition, three concentrations (1%, 2% and 3% based on oven dried weight of the pulp) of PVC were applied along with various mixtures of dry strength additives to compare the results. In the case of mixture, 6 different orders of polymers with dosages of 0.5% chitosan, 0.5% cationic starch and 1% PVA were used. Different dosage solutions of additives were added to a 1000 mL of stock at 3% consistency of unbeaten OCC pulp. The mixture was agitated for 20 min at room temperature (25 °C). In the case of mixture of additives, after addition of each agent the suspension was mixed for 3 min and other additives were then added. Subsequently, the suspension was diluted with distilled water to 0.5% consistency.

2.3. Sheet formation and paper testing

After mixing the pulp suspension, handsheets with target weight of 100 g/m² were made in a British handsheet former as per TAPPI Standard T 205 sp-02. For determination of dry strength properties, the samples were conditioned at 50 ± 2% relative humidity and 23 ± 1 °C temperature according to TAPPI T 402 sp-98 for at least 4 h and then, the dry tensile and stretch properties of handsheets were tested according to ISO 1924-2. Five replications were tested for each treatment.

For wet strength, the tensile and stretch properties of preformed (treated) handsheets were determined according to ISO 1924-2, just after they were removed from the sheet mold. At this point the sheet contains about 30–60% solid content. More than twenty replications were tested for each treatment and dry solid content of all samples was determined by weighting the samples in wet and dry states.

It is also worth mentioning that an exponential function was fitted to data from strength responses obtained from employing the combined polymers and strength response normalized to a constant dry solid content for analysis. In order to simplify the experiments no other additions, such as alum and AKD, were added to the slurry.

3. Results and discussion

3.1. Effect of polymers on paper properties

Data on wet tensile and stretch properties of sheets treated by four distinct polymeric additives are presented in Figs. 2 and 3, whereas Fig. 4 shows the same properties in dry condition. In general, the addition of additives in any concentrations considerably enhanced tensile strength of the handsheets in wet and dry conditions, compared with the untreated ones (control). The results demonstrate that the addition of both types of chitosan can increase both wet and dry tensile strength remarkably. In addition, chitosan application has a unique effect on the strength property compared with cationic starch and PVA treated papers; for instance, at 1%

dosage of chitosan II, the increase in tensile strength was about 40% more than the control sample. A similar trend was observed for chitosan I treated samples (Fig. 2a). However, the increase beyond 0.75% was less. Increasing the concentration of chitosan from 0–0.75% resulted in 15–25% gain in strength, but adding more chitosan (i.e. 0.75–1.0%) gave only about 10% increase in strength properties comparing to 0.75% chitosan addition (Fig. 2b). This indicates that chitosan should be used based on end-product quality requirements and the cost effectiveness of the process. These results are in good agreement with previous findings using chitosan (Lertsutthiwong et al., 2004; Ashori et al., 2006). The differences in the performance of employed chitosans is presumably due to the differences in the polymer molecular weight, while longer chitosan (Ch I) produces further contacts between fibers than shorter chain chitosan (Ch II).

Dry tensile properties increased when the above-mentioned additives were added to the pulp furnish. Similar to wet condition, the effect of chitosan with low concentrations (0.25–1%) on the tensile properties of handsheets was better than other additives (Fig. 4a and b). For instance, at 1% chitosan addition, the increase of dry condition in tensile index and stretch were about 22% and 7% more, respectively, than the corresponding increases under wet conditions. This can be explained by the fact that chitosan can enhance the internal bonding strength of paper by creating additional bonds. As the ionized amino groups of chitosan come into contact with fibers, in the presence of water they can form ionic and imino bonds (Fig. 5). The mechanical properties of paper depend on inter-fiber bonding, and so it is most probable that chitosan exerts its beneficial effects on paper by increasing the inter-fiber bond strengths. The structural configuration of chitosan might explain some of the differences in performance when compared with PVA and cationic starch. The primary chemical structures of chitosan and PVA are linear polymer chains, while starch is composed of amylopectin, which is branched. Starch has α -linkage, which causes it to take helical form, while chitosan has β -linkage, which translates it into straight molecular chains. These chains are more conformable, which facilitate accessibility of their functional groups for bonding to a cellulose surface. Furthermore, both chitosan and cationic starch possess amino or ammonium groups, which give a strong cationic character to chitosan and cationic starch, while PVA does not contain this functionality. PVA is non-ionic in character. Amide bonds may also develop during drying. Such interactions would improve the internal bond strength and resistance of paper to water (Laleg & Pikulik Ivan, 1993).

Figs. 3 and 4 show the stretch to rupture of handsheets produced by following treatment with chitosan, cationic starch and PVA in wet and dry conditions, respectively. In wet case, the results demonstrate that the stretch values of treated samples at breaking point were less than the control, however with increasing the concentration of additives, stretch was improved. For instance at 35% dryness, the stretch values were 1% and 1.5% for dosages of 0.5% and 1% chitosan treated samples, respectively. Similar stretch behavior took place in the wet condition for all additives (Fig. 3),

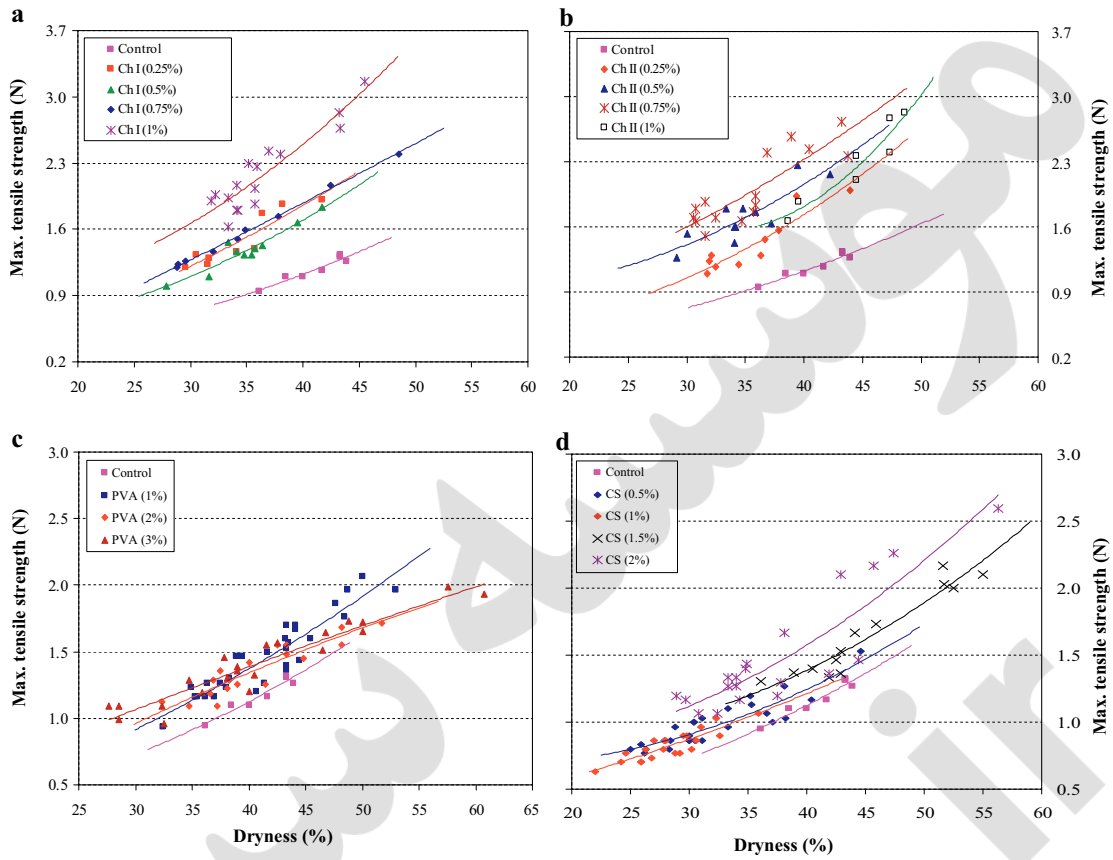


Fig. 2. Effect of increasing additives content and dryness on wet tensile strength.

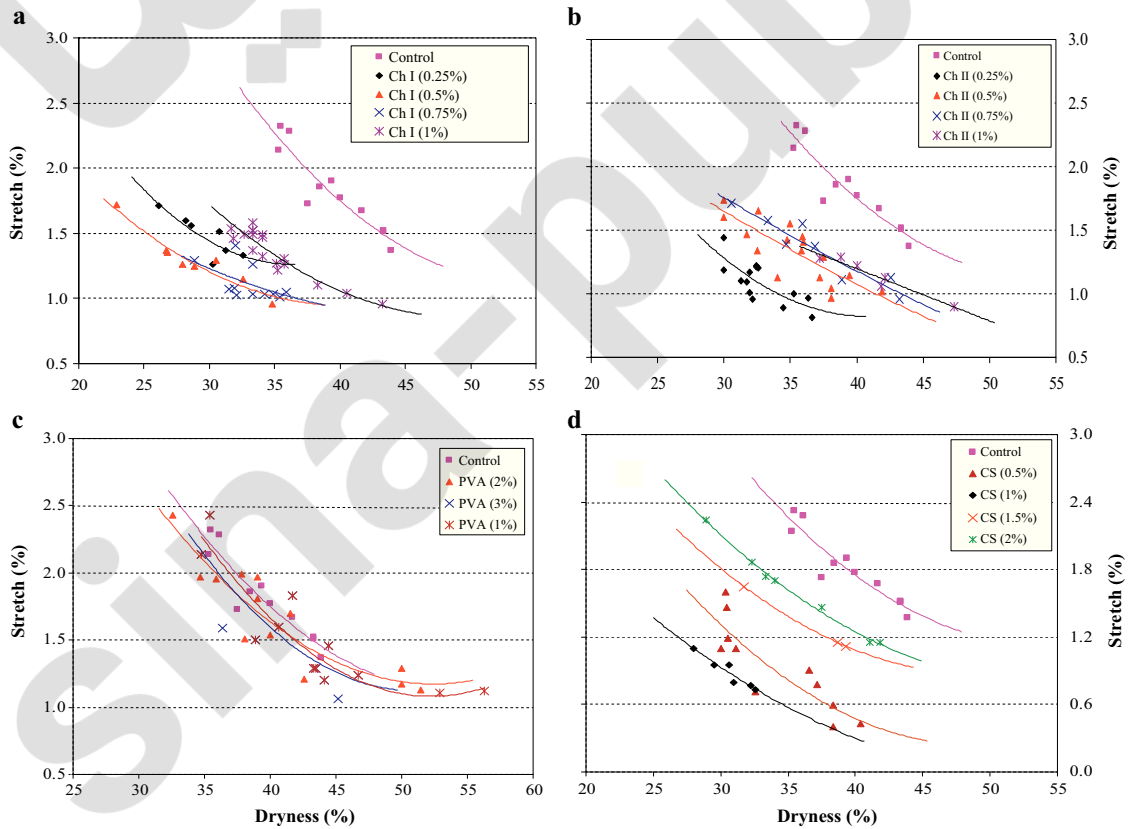


Fig. 3. Effect of increasing additives content and dryness on wet stretch property.

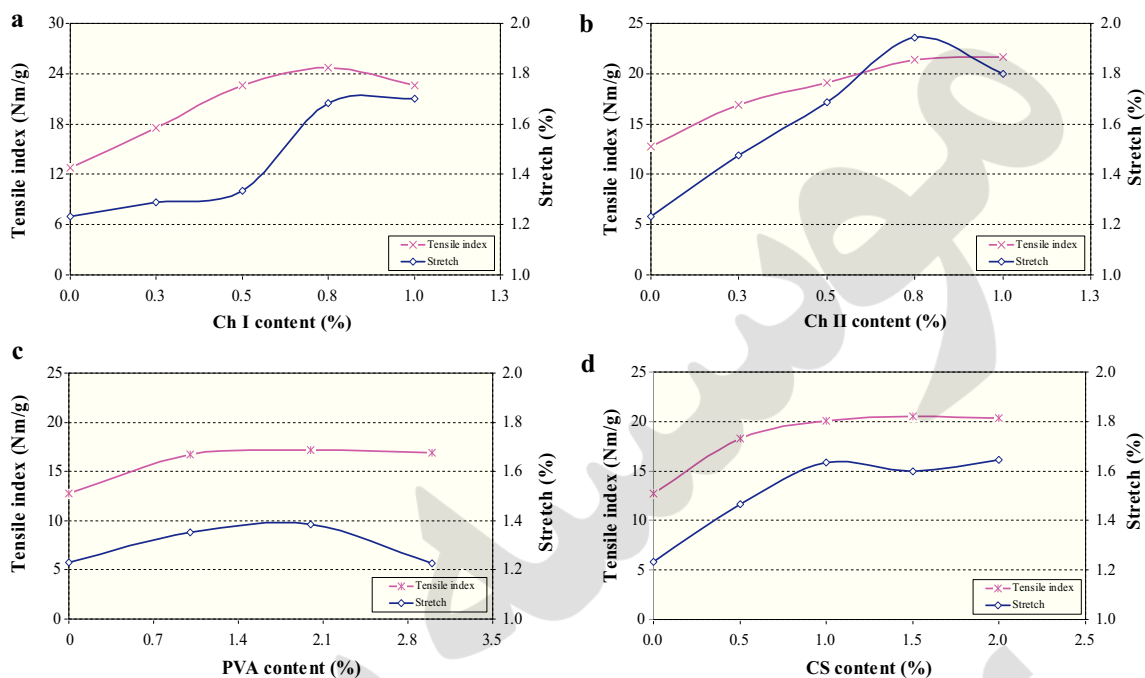


Fig. 4. Effect of increasing additives content on dry tensile and stretch properties.

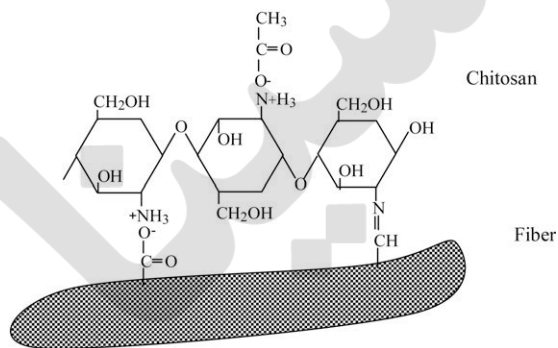


Fig. 5. The formation of ionic and imino bonds between chitosan and pulp fibers.

but, chitosan I and II with the lowest concentration could show the highest stretch values. As mentioned earlier, the reason for this phenomenon is attributed to the differences originating from the chemical nature.

In contrast to the wet conditions, all treated samples showed superior stretch values at dry condition compared with control (Fig. 4). In case of PVA, the increase in stretch was significantly lower than cationic starch and chitosan treated papers. Once again, chitosan treated papers with the lowest concentration had the highest values. As in the case of cationic starch, the effect was higher when the dosage of polymer was higher.

3.2. Effects of sequential polymer addition

In this work, various sequences of polymeric additives were examined to find the optimal combination for improving both wet and dry strength. Figs. 6 and 7 show the tensile and stretch properties of handsheets produced at wet and dry conditions, respectively. In general, the addition of polymers in any sequences considerably increased tensile strength of the handsheets compared with the untreated ones (control). This indicated that the dry strength properties of OCC pulp were significantly improved when the pulp was treated by all sequential chemical additions. However, the

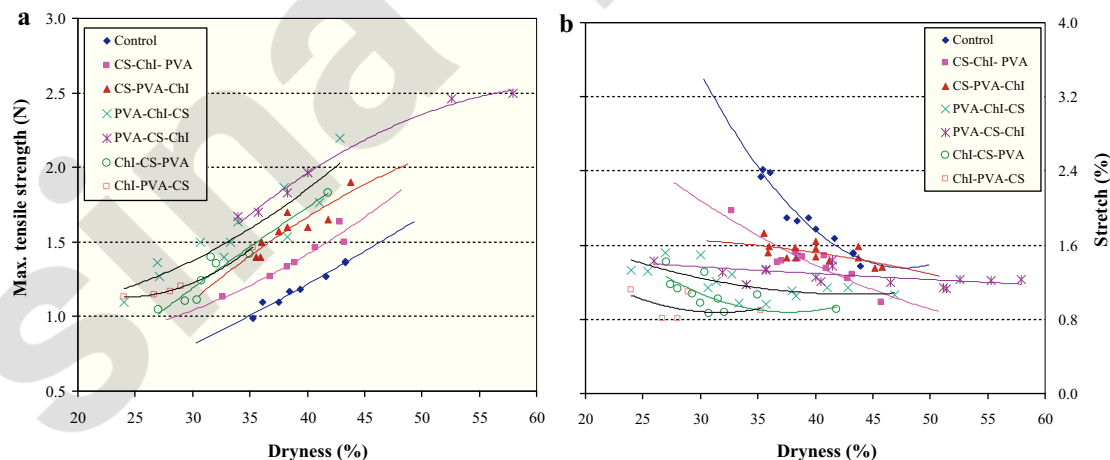


Fig. 6. Influence of sequential polymer addition and dryness on wet tensile and stretch properties.

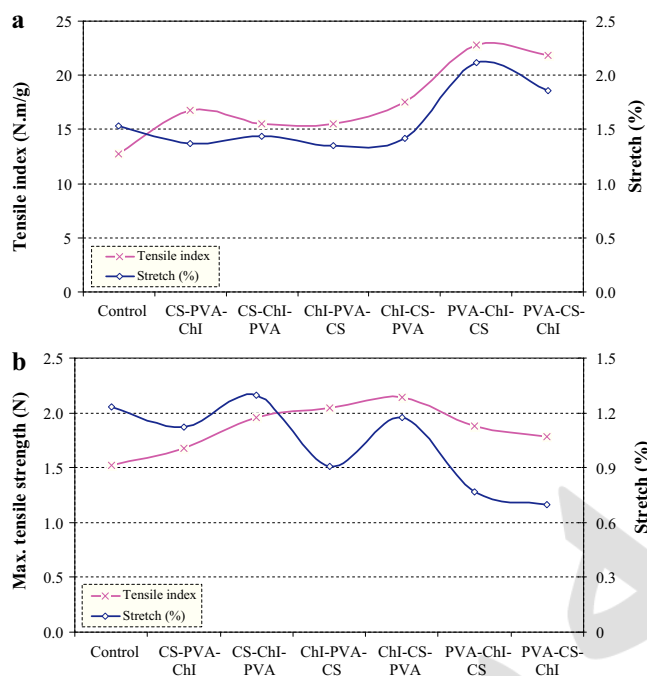


Fig. 7. Influence of sequential polymer addition on dry (a) and wet (b) tensile and stretch properties.

sequence of PVA-Chl-CS and followed by PVA-CS-Chl showed the superior results for both wet and dry conditions. As it can be seen from Fig. 7, the enhancing effect of additives on dry tensile index is much higher than wet condition.

Because of a significant correlation between wet web break and combined wet web strength and stretch (Uesaka & Ferahi, 1999), the potential of chemical treatments to enhance the runability of wet web in paper machine was estimated based on the combined factor of (tensile strength and stretch^{0.5}). In Fig. 7, sequential treatment of fiber by PVA-Chl-CS and followed by CS-PVA-Chl showed clearly better results, since they have both produced higher tensile strength and caused lower reduction in stretch compared to the control.

Kataja-aho et al. (2012) reported that sequential addition of oppositely charged polymers forms a macromolecular layered structure of polyelectrolytes; so-called polyelectrolyte multilayers (PEM). The PEM have been found to increase the molecular contact area in the fiber–fiber joints. It has also been found that these multilayers create a larger number of fiber–fiber contacts in the sheet. The use of polyelectrolyte multilayers has been shown to increase dry-paper strength with only a minor reduction in density, light-scattering, or the formation of the sheet. The increase in strength has been demonstrated to be largely dependent on the adsorption of these polymers, which is affected by several parameters, such as electrolyte concentration, the type of electrolyte, and the charge density (Salminen et al., 2011).

4. Conclusions

The use of recycled fibers is steadily increasing in various paper products and there is a need to improve the strength properties of paper products made from these fibers. Using a dry strength additive is a potential solution. Hence, in this study some polymeric additives were used to enhance tensile strength of OCC recycled paper. Some conclusions of addition of dry strength agents are as follows:

- Tensile properties for specimens treated with all types of additives were generally higher than untreated ones (control).
- The addition of chitosan had more positive effects on the tensile strength, compared to sheets treated with cationic starch and PVA.
- The addition of chitosan increased both wet and dry tensile strength remarkably. However, the rate of increase was higher from 0 to 0.5% compared to 0.75–1% regardless of the molecular weight.
- Convincing results demonstrated that high molecular weight chitosan (Ch I) performed more efficiently on wet and dry strength enhancements of papers.
- The stretch values of the sized papers moderately decreased, however it was improved with increasing the dosage of additives.
- These materials bond well to the fiber surfaces and are capable of bridging inter-fiber distances, thereby establishing bonds between fibers and fibrils that would not have otherwise formed.
- Dry tensile property was significantly improved with sequential polymer addition. The optimal sequence was found to be PVA-Chl-CS.

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