Performance of Fixing Agents in Controlling Micro-Stickies in Recycled Newsprint Pulp

WANG LI-JUN*, CHEN FU-SHAN†, and ZHOU LIN-JIE‡

*Professor, †Professor, ‡Master Student
Tianjin Key Lab of Pulp and Paper, Tianjin University of Science & Technology, Tianjin, 300222, China
wangchem@tust.edu.cn

ABSTRACT

The microstickes control effects of some fixing agents, including an inorganic PAC, an organic polyamine (PA) and polydiallydimethyl ammonium chloride (Pdadmac), and a high cationic starch (HCS), were investigated, together with their effects on wet end performances and physical properties of handsheets. Despite that the HCS and Pdadmac had lower cationic charge densities than the PA and PAC (the HCS being even lower), they gave higher zeta potentials to fibers, and lower turbidities, cationic demands and residual COD contents to the pulp liquid phases than the PA and PAC did. In all cases, the HCS showed even better effects than the Pdadmac. In addition, drainage speed was also much higher by the HCS treatments although paper formation was worsened. All the phenomena showed that the HCS can fix more dissolved and colloidal substances to cellulose fibers, indicating that the HCS functioned mainly with flocculation and even hydrogen bonding mechanisms. Data on optical properties further indicated that the HCS interacted preferentially with colloidal substances, since it fixed more "dirty" microstickes to fibers which decreased more sheet brightness while increasing more sheet opacity (with both higher light absorption and scattering coefficients). Interestingly, the organic fixing agents did not decrease tensile, tearing, and folding strengths of paper sheets made from 100% recycled newsprint pulp, except when they were dosed in high amounts. On the contrary, the inorganic PAC had more serious negative effects on the strength properties, especially on folding endurance. The study suggested that proper use of the HCS can lead to better microstickies control effects than traditional agents and methods.

INTRODUCTION

Paper recycling is very important in reuse of natural fiber resources and improving environmental protection. However, stickies control is a difficult task during the use of recycled pulp. Stickies include all the tacky, soft and hydrophobic organic materials produced in the recycling process, they mainly come from tapes, label adhesives, hot melts, waxes, ink binders, latexes, wet strength agents and other polymeric materials. According to difference in sizes, they are divided into macrostickies and microstickies, generally a slot screen determines this classification, that is, those retained by the screen with 0.15mm slots are macrosticies, and those pass are microstickies. A small part microstickies are actually shattered from macrostickies, but the main are dissolved and colloidal substances (DCS). Due to sudden changes of temperature, local concentration, shearing, pH and chemicals environments, the DCS can easily be destabilized, and accordingly, a part of the dissolved substances may precipitate out to be new colloidal substances, and a part of colloidal substances may agglomerate into bigger ones and deposit onto wires, press felts, suction rolls, uhle boxes, dryer surfaces and paper webs, causing process runnability problems and lowing paper quality. Currently, chemical and microbial methods are used to control microstickies. The principles include dispersion with dispersants, adsorption onto less tacky particles, passivation of machine surfaces with surfactants, decomposition into smaller particles and detackification (the enzyme method), fixation onto fibers by fixing agents, etc [1]. The fixing method, i.e., using fixing agents (polyelectrolytes with relatively low molecular weights and high cationic charge densities) to fix dissolved and colloidal substances onto paper fibers and take them out of papermaking system, is an easily applicable and widely used method [2]. However, different fixing agent may have difference performances, because they differ in various aspects such as molecular weight, charge density, conformation, ability of detackification, etc. Mills always faces problems of screening out a good fixing agent before it is tried on the giant paper machine [3]. Our research focused to give helps to such needs. In addition, considering that our country is in lack of fresh fiber resources and as high as 52% of the whole pulps used in China was occupied by secondary fibers, we are interested if HCS or HCG (high cationic gum) can be used successfully as "new" fixing agents in papermaking with 100% recycled paper was of great concern to us. It was thought that due to their very good hydrogen bonding ability with cellulose, HCS or HCG might still have some dry strengthening effect even after they act as fixing agents. However, being time limited, this paper only focused on the effects of different fixing agents (PAC, PA, Pdadmac, HCS, but without HCG) on the wet end and physical properties of paper made from the recycled newsprint.

EXPERIMENTAL

Raw materials

The pulp was made from 100% waste old newspaper, it was sampled from the machine chest of a newsprint line in Tianjin, China., no wet end chemicals had been added at this place. Polyalluminum chloride (PAC) was from Nanning Chemical Co. Ltd., China. Polydiallyldimethyl ammonium chloride (Pdadamac) was from Alim Corporation, Korea. Polyamine (PA) and high cationic starch (HCS) was synthesized by our own laboratory, was prepared in our own laboratory. The charge densities of the above chemicals were 4.33, 3.67, 5.83 and 0.49 meq/g solid, respectively for the PAC, Pdadmac, PA and HCS.

Methods

Investigating the effects of fixing agent on wet end performances

The fixing agents were added to the newsprint pulp (consistency 4.8%) directly with good stirring for 3minutes. Then the pulp was diluted to 0.5% consistency. SZP06 (BTG Co. Ltd) was used to measure the zeta (ξ) potentials of the treated and untreated fibers. DFR04 (BTG Co. Ltd.) was used to measure the pulp drainage properties. The filtrations from the DFR04 were collected, centrifuged at 2000rpm for 20minutes, and the turbidities of the supernatants measured with a LP 2000-11 turbidity meter (Hanna Instrumental Co. Ltd), cationic charge demands with a PCD03 particle charge detector (BTG Co. Ltd.), and COD values with 10minutes rapid method. Considering that no filler was used in making the newsprint in the mill, retention was not measured in this study. Direct flocculation behavior such as floc sizes could not be measured in our laboratory, but it was studied indirectly by measuring the formation index with a 2D Lab Formation Sensor (Techpap Co. Ltd., France) after handsheet forming.

Investigating the effects of fixing agent on paper properties

Handsheets with a basis weight of $60 g/m^2$ were made with a standard sheet former (Canada Labtech Instruments Co.). The brightness, opacity, light scattering and absorptive coefficients were measured with a L & W Elrepho Routine SE 070R spectrophotometer. Handsheet strength properties were measured according to the Tappi standard methods. T-test statistical analysis method was used to compare the strength data. This method tells whether real differences exited between the fixing agent treated samples and the untreated one (the control), judging from the "p-value", a p-value less than 0.05 means the difference is significant, while a larger one not [4].

RESULTS AND DISCUSSION

Effects of fixing agents on wet end performances of pulp

dissolved and colloidal substances is the main source of microstickies generation, its content can be generally inferred from the turbidity, cationic demand and chemical oxygen demand (COD) of the pulp filtrate [5-6]. Here we measured the pulp ξ potentials, dynamic drainage properties of pulp, turbidities, cationic demands, and COD values of pulp filtrates, and at last indirectly the handsheet formation indices, to investigate the effects of fixing agents on papermaking wet-end performances.

Different amounts of fixing agent were added to the recycled newsprint pulp. From fig. 1 it was seen that adding the same amount of cationic charges, HCS increased much higher fiber ξ potentials than the other three fixing agents did. The Pdadmac had a little higher effect than the PA and PAC, while the PA and PAC was very similar, and their ξ potential increases were small. Theoretically, increase of ξ potential is due to the adsorption of cationic polymers onto the fibers. Therefore, it indicated that HCS had much higher affinity with fiber than the other three fixing agents. Remember that the HCS had much lower charge density than the other three (see experimental), this high affinity was thought to be from two mechanisms. One is that the HCS has good hydrogen bonding with the cellulose fibers, the other is that the HCS might have behaved like a retention agent, since it is very possible that the starch had much high molecular weight than the other fixatives. Additionally, the PA and PAC seemed to neutralize, coagulate the anionic trashes in the pulp suspension and fixed them to cellulose fibers, no doubt the Pdadmac had stronger coagulation and fixing effects.

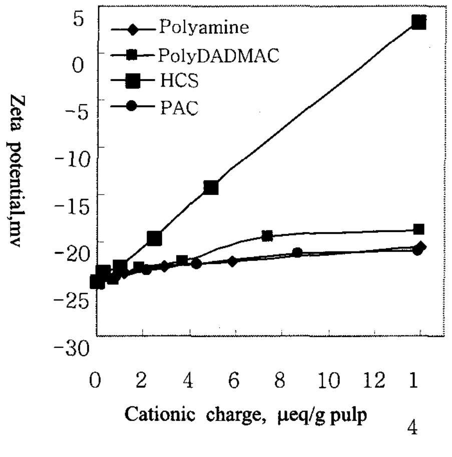

Fig. 1 Fixing agent on ξ potentials of pulp fibers

The Effects of fixing agents on cationic demands were shown in figure 2. In all cases, the increase addition of fixing agents decreased the cationic demand of pulp filtrates, however, the effect was again in the order of HCS>Pdadmac>PA ≈ PAC, much the same as that shown in ξ potentials. Interestingly enough, the relationships of PA and PAC with the cationic charge were almost linear. This gave certain proof that the PA and PAC functioned with a neutralization and coagulation mechanisms while the Pdadmac and HCS had some flocculation effects, or else the latter two would not give out bend curves. One mole equivalent of Pdadmac and HCS adsorbed more than 1 mole equivalents of anionic dissolved and colloidal substances. That the HCS was more beyond a stoichiometric relationship may be ascribed to its additional hydrogen bonding with cellulose fibers.

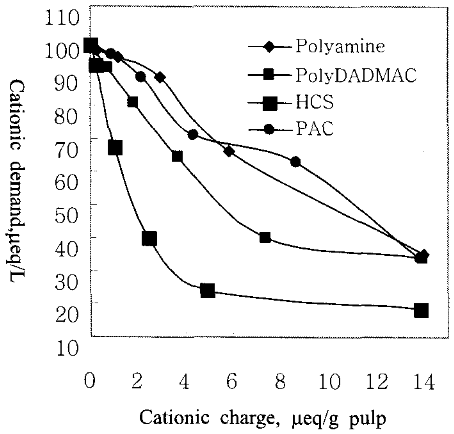

Fig.2 Fixing agent on cationic demands of pulp filtrates

The effects of fixing agent on turbidities of pulp filtrates were shown in figure 3. In all cases, the turbidities decreased sharply with the increase addition of fixing agents. At a cationic dosage of 14.0μeq/g pulp, the PAC, PA and PDADMAC decrease the turbidity by 84.6%, 82.4%, and 90.3% respectively. 92.7% reduction in turbidity was achieved by HCS at the dosage of 4.9μeq/g pulp. This indicated that all the fixing agents had good performance in removing colloidal substances in the pulp slurry, but HCS was much better than the other three, while Pdadmac was slightly better than the other two. Again it can be thought that if the PA and PAC mainly functioned with the mechanisms of neutralization and coagulation, the Pdadmac and HCS might function with some flocculation mechanism, and that the HCS had higher effect might be ascribed to its hydrogen bonding ability.

An interesting phenomenon in figure 3 showed that high dosage of HCS slightly increased the turbidity again (a typical phenomenon seen in charge reversal). Since the charge density of HCS was much less than the other fixing agent, it was impossible for it to function in a neutralizing mechanism (neutralized state can be reached faster by the other three fixing agent). Therefore, the HCS must have functioned in a flocculation mechanism. In this way, the HCS can collect more colloidal substances with much less cationic charge. This effect was so great that it not only successfully attached to fibers, increasing pulp ξ potential as seen in figure 1, but also made the colloidal substances cationic, i.e., a charge reversal and a rebound of higher turbidity.

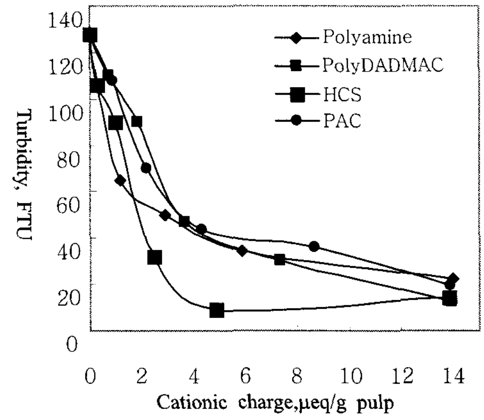

Fig. 3 Fixing agents on turbidities of pulp filtrates

The effects of fixing agents on COD values of pulp filtrates were shown in figure 4. With the increase addition of fixing agents, COD decreased. Again HCS showed the largest effect. However, say collectively, even in the best case, only 15-20% of COD was reduced. J. Y. Lee et al. reported a similar result when they were investigating the adsorption of a cationic guar gum with a degree of substitution of 0.1 on fibers [7]. It seemed that most of the dissolved and colloidal substances successfully removed by fixing agents was not was not cod components. Why it is so will be carried out in our other researches by a through identification of the composition of dissolved and colloidal substances.

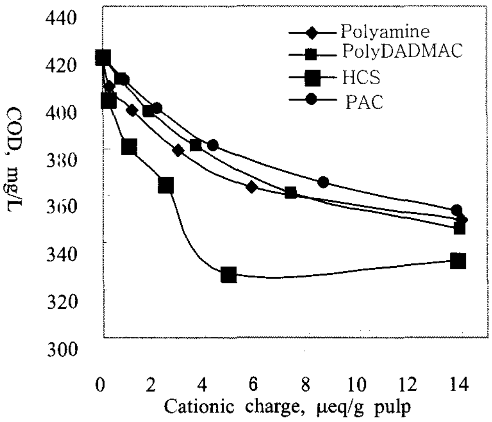

Fig. 4 Fixing agents on COD values of pulp filtrates

Figure 5 showed the effects of fixing agents on pulp drainage properties. PA and PAC treatments improved the dynamic drainage rates of pulp very slightly, indicating that fixing the dissolved and colloidal substances onto fibers had very little help on improving drainage. In this point, A. J. Dunhan et al. reported that neutralization of DCS retarded drainage [8]. Good drainage can be achieved by Pdadmac, which maybe caused by partial flocculation of fibers. HCS also showed good improvement in dewatering, however, when its dosage was higher than 4.9 μeq/g pulp (around 1.0 wt % on oven dried pulp), the improvement in drainage deteriorated dramatically. This was thought to be caused by higher viscosity of pulp filtrate in high dosage of the HCS.

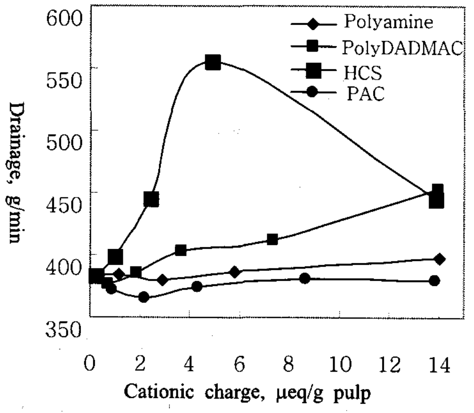

Fig. 5 Fixing agents on pulp drainage properties

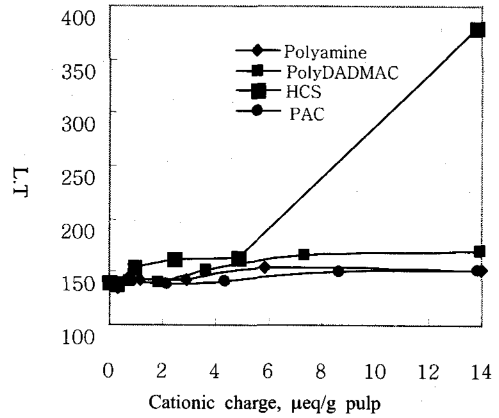

Fig. 6 Fixing agents on fiber flocculation

The measurements of formation indices after the pulps were made into sheets gave further proof that the flocculation effects caused by the fixing agents were in the order of HCS>Pdadmac>PA>PAC. In figure 6, L.T (look through) was an integrated formation index, higher values mean worse formation. It was also seen that special attention should be paid to HCS, which worsened formation dramatically when the dosage was over 5.0μeq/g pulp. In real application, its dosage must be kept under this deadline (around 1% on oven dried pulp).

Effects of fixing agents on paper properties

Effects of fixing agents on sheet optical properties

Figure 7 showed that with the addition of cationic fixing agents, paper brightness decreased significantly. This was because a great deal of colloidal substances in recycled ONP was dark colored. On the other hand, the dissolved substances were almost colorless because clear filtrates can be obtained if filtered through a 1.2 μm glass fiber paper. Since the HCS treatments had much greater effect on brightness drop than the other treatments, it again gave evidence that the HCS greatly flocculated the colored colloidal substances in the pulp. This is also the reason why opacity was increased greatly by HCS as was seen in figure 8. Further study showed that the increase of opacity was caused by both increase in paper light scattering coefficient and light absorption coefficient (figures not shown). The negative effects on brightness might be compensated from slight amount of white pigment addition (such as GCC or PCC) and better bleaching.

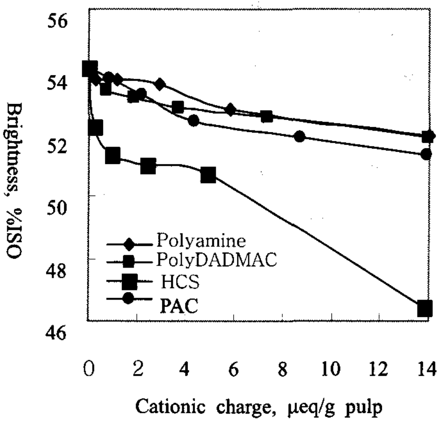

Fig. 7 Fixing agents on paper brightness

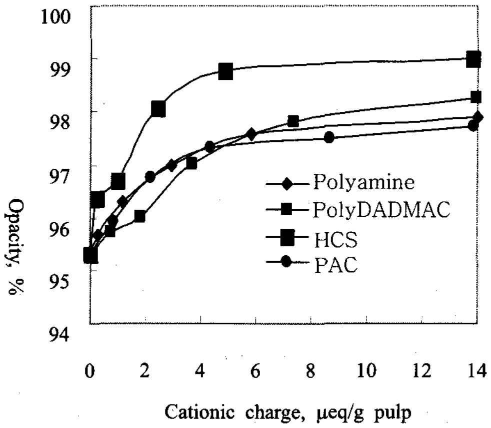

Fig. 8 Fixing agents on opacities of paper sheets

Effects of fixing agent on sheet strength properties

Table 1 showed the effects of the four fixing agents on paper strength properties including tensile index, tearing index and folding index. All the data were only compared with those of the control. As stated in the experimental, only the data with p-values less than 0.05 mean that the differences between the samples and the control are statistically significant. After determining which treatment had significant difference with the control, the mean values between the control and the treated sample was compared, then whether the treatment decreased or increased the property was known.

Interestingly, table 1 showed that addition of PA, PDADMAC, and HCS had no significant effect on tensile and tearing strengths. Only when their dosages were at high levels did they show some deteriorating effect on tearing strength. This is very different to the research results where mechanical pulps were used, where DCS fixation deteriorated strength properties [9-10]. The detrimental effects of DCS on paper strengths seemed to appear much less on 100% recycled ONP than on thermo-mechanical pulps, the reason might be ascribed to different nature of the pitch materials in mechanical pulps and the stickies materials from recycled papers. Many stickies components are high molecular polymeric materials that may contribute to strength development like internally added latex [11] to fibers.

It is also interesting to see that the inorganic PAC decreased paper strengths more clearly than the above three organic polyelectrolytes. Especially the effect of PAC on fold endurance was dramatic.

CONCLUSION

For the four kinds of fixing agents investigated in this study, the high cationic starch (HCS) had better affinity to cellulose fiber than the other fixing agents even if it had the very lowest charge density. At the same dosages of cationic charges, the HCS removed much more dissolved and colloidal substances than the Pdadmac, PA and PAC. Pdadmac was also significantly better than the PA and PAC, but PA was only slightly better than PAC. Many facts inferred that the HCS controlled microstickies mainly by flocculation and also possibly hydrogen bonding mechanisms.

Fixation of micristickies components to fiber deteriorated paper brightness while increasing opacity. Surprisingly, fixing the dissolved and colloidal substances in the 100% recycled pulp did not retard the corresponding paper strength development as severely as the cases for mechanical pulps reported by literatures. Under reasonable dosages, tensile and tearing strengths were not affected, but tearing was affected more easily. In this point, inorganic PAC was worse than the organic HCS, Pdadmac and PA.

As a matter of fact, one purpose of using fixing agents is to save more expensive retention aids in the wet end. High cationic starch was made partially from starch natural polymer, so it is much cheaper than those widely used PAM retention aids. Therefore, even if the HCS performed much like a flocculant, we believe it still can be used as a microstickies "fixing agent".

We also think that traditional fixing agents can be used together with the HCS to improve the microstickies control effect. In addition, whether hydrogen bonding really improved microstickies control effects might be further inferred from the use of high cationic guar gum (HCG), because guar gums were known to have higher hydrogen bonding ability than starches. These two points are still under our further studying.

REFERENCE

[1] Thierry Delagoutte, Josiane Brun and Bruno Carre, Recent Advances in Paper Recycling – Stickies, Ed. Mahendra R. Doshi, 134-139, Doshi & Associates, Inc. (2002).
[2] Leio Neimo. Papermaking Chemistry, Papermaking Science and Technology, Ed. Johan Gullichsen and Hannu Paulapuro, 235-236, Fapet Oy (1999)
[3] Larry H. Allen and Denise Filion, A laboratory white pitch deposition test for screening additives, Tappi Journal, 79 (2): 226 (1996)
[4] Douglas C. Montgonery, Design and Analysis of Experiments, Ed. Douglas C. Montgonery, 34-41, John Wiley & Sons (1999)
[5] Tapio Vihervaara, Jouko Käki. A new generation of starch based cationic polymers for controlling wet end chemistry, 1994 Papermakers Conference, Tappi Proceedings: 524 (1994)
[6] Anna Sundberg, Rainer Ekman, Bjarne Holmbom, Interaction between dissolved and colloidal substances and a cationic fixing agent in mechanical pulp suspensions, Nordic Pulp and Paper Research Journal, 8 (1): 226 (1993)
[7] J. Y. Lee, H. K Lee and H. J. Youn, Adsorption analysis of cationic guar gum on fibers in closed papermaking systems, Tappi Journal, 4 (10): 15 (2005)
[8] A. J. Dunham, L. M. Sherman and J.C. Alfano, Effects of dissolve and colloidal substances on drainage properties of mechanical pulp suspensions, Journal of Pulp and Paper Science, 28 (9): 298 (2002)
[9] D.W. Francis and M. D. Ouchi, Effect of dissolved and colloidal solids on newsprint properties, Journal of Pulp and Paper Science, 27 (9):289 (2001)
[10] Seila Tay, Effects of dissolved and colloidal contaminants in newsprint machine white water on water surface tension and paper physical properties, Tappi Journal. 84 (8): 1 (2001)
[11] Bob Alince, Cationic latex as a multifunctional wet-end additives in highly filled paper, Tappi Journal 3 (1): 16 (2004)

APPENDICES

Table 1. Effects of fixing agent on mechanical properties of paper sheets

Fixing agent	Dosages (%odp)	Tensile Index		Tearing Index		Folding Index	
		Mean (N.m/g)	p-value	Mean (mN.m^2/g)	p-value	Mean (m^2/g)	p-value
Blank	0	36.57	1.000	5.97	1.000	0.27	1.000
PAC	0.02	37.11	0.696	6.00	0.907	0.24	0.275
	0.05	34.92	0.229	5.72	0.248	***0.15***	***1.68×10^{-4}***
	0.10	35.65	0.476	5.63	0.068	***0.12***	***4.20×10^{-5}***
	0.20	***30.93***	***0.001***	6.11	0.597	***0.12***	***1.53×10^{-4}***
	0.32	***32.23***	***0.006***	***5.19***	***0.001***	***0.14***	***1.07×10^{-4}***
PA	0.01	38.87	0.119	6.06	0.697	0.26	0.873
	0.02	38.81	0.249	5.96	0.956	0.32	0.160
	0.05	38.06	0.266	5.86	0.525	0.23	0.252
	0.10	37.46	0.505	6.37	0.060	0.27	0.867
	0.24	34.92	0.209	6.25	0.255	*0.19*	*0.007*
PDADMAC	0.02	39.20	0.069	6.15	0.499	0.23	0.123
	0.05	38.92	0.111	5.89	0.751	0.27	0.852
	0.10	38.05	0.284	5.35	0.052	0.23	0.164
	0.20	35.75	0.529	5.85	0.516	***0.16***	***3.80×10^{-4}***
	0.38	34.51	0.133	5.75	0.347	***0.14***	***7.00×10^{-5}***
HCS	0.05	37.68	0.441	6.36	0.260	0.29	0.483
	0.20	36.61	0.977	6.27	0.360	0.24	0.221
	0.50	35.96	0.623	5.96	0.941	***0.19***	***0.014***
	1.00	34.88	0.336	5.66	0.068	***0.16***	***0.001***
	2.85	-	-	-	-	-	-

Note: p-values less than 0.05 and their corresponding mean values were showed in bold and italic.