

## PHYSICOCHEMICAL PROPERTIES ANALYSIS AND SIZE DISTRIBUTION RESEARCH OF MICROSTICKIES IN WHITEWATER

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Microstickies in whitewater have caused serious deterioration of paper quality and low efficiency of paper machine runnability. To solve this problem it is necessary to master the characteristics of various aspects of microstickies. In this study, the physicochemical properties and size distribution of microstickies in whitewater of three typical kinds of waste papers, old newspaper (ONP), old book paper (OBP), and mixed office wastepaper (MOW), were investigated by conventional methods and a modified Flow Cytometry Method (FCM). The results showed that white water microstickies in different kinds of waste paper have different characteristics. This is a premise for analyzing stickies problems. Furthermore, in a certain kind of waste paper, the physicochemical properties and the direct determination of size and number of microstickies particle in whitewater can be combined together and taken as a whole to account for more phenomena or deduce more mechanisms, such as agglomeration and deposition, *etc.*

*Keywords:* Microstickies; Whitewater; Physicochemical; Size distribution; FCM

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### INTRODUCTION

In waste paper recycling, stickies refer to the tacky contaminants (Sarja 2007), and they are usually divided into two types according to the particle size: macrostickies (>100 µm) and microstickies (<100 µm). Most of the macrostickies can be removed effectively by the processes of screening with 0.1 mm screen slots (Francois *et al.* 2005). However, it is hard to remove a large amount of microstickies (Gruber *et al.* 1998) in the units of pulping since they are too small and have complicated features. These microstickies would be retained in the pulp and introduced into the papermaking system, causing serious deterioration of paper quality and paper machine runnability (Goto *et al.* 2007). As a result of problems with microstickies, especially adhesive contaminants in whitewater, increasing attention is being paid to measurement and control.

Many quantitative methods of microstickies have been developed and researched, such as solvent extraction (Donald *et al.* 2010), UCM deposition testing (Doshi *et al.* 2003a), the IPST (TOC) method, the “pitch-counter” method (Hamann *et al.* 2004; Künzel and Prinz 2006; Huo *et al.* 2001), the PAPRICAN thermogravimetry method (Doshi *et al.* 2003a), the TAPPI method (Jong *et al.* 2006), the Pulmac macro/microstickies classifier (Doshi *et al.* 2008), MVStick 600 NIR (Near infrared spectroscopy) (Hodges *et al.* 2006; Leon and Millvision 2009), the QCM method (Quartz Crystal Microbalance) (Goto *et al.* 2007), and the HS-GC method (Chai *et al.* 2007), *etc.*

Though all of these methods attempt to obtain the quantity information of microstickies in white water, most of them are indirect and cannot test all of the content of microstickies. Also, no information of the size and number of microstickies particles can be measured by these above methods.

On the basis of these current methods, many studies on the control, agglomeration, and deposition of microstickies have been investigated. Wang *et al.* (2006; 2007) researched the performance of fixing agents in controlling microstickies with the conventional measurement for white water. Banerjee and Daniel (2008) studied the effect of cyclodextrins on the tack of stickies via a tack tester and an atomic force microscope. Besides, De Jong (2005) conducted the change of macrostickies converted from microstickies to analyze the agglomeration of microstickies particles. Banerjee *et al.* (2009) tracked the change in particle size of microstickies to study the deposition phenomena through the effective measurement of micro-organic accumulation method. Castro and Dorris (2004) modified a dynamic drainage jar (DDJ) to monitor the rate of deposition of microstickies by testing the pressure loss across the wire. And Li (2011) applied pectinase for reducing stickies deposition with the method of measuring the content of dissolved and colloidal substances (DCS).

In recent years, a novel laser particle analyzer called Flow Cytometry (FCM) was introduced from the medical science field to the papermaking industry. The measurement principle of this method is based on the accurate detection of fluorescence particles of small size and can distinguish stickies from non-stickies. This method was applied by BASF-Canada in colloidal stickies measurement (Klungness 2002). Then Vähäsalo *et al.* (2003) applied it for on-line wet-end chemistry research, revealing a very clear correlation between starch aggregates and deposits onto papermaking equipment. Then CIBA (Switzerland) improved the method and named this device the Ciba Contaminant Analyzer (CAA), of which the detection ranges were extended and can cover 0.1 to 100  $\mu\text{m}$ . The device also can be used to test the efficiency of fixative, the number of residual colloidal contaminants and their relative particle sizes in pitch control (Chen *et al.* 2007). However, the accurate quantitative information of microstickies in white water, such as the particle size distribution, has not been directly measured by this method, since the capability of normal FCM cannot achieve.

In this study, the physicochemical properties and size distribution of microstickies in three kinds of waste paper were investigated by conventional methods, and a modified FCM combined the application of a kind of fluorescent sticky control reagent and standard model microballoons.

## EXPERIMENTAL

### Materials

Old newspaper (ONP) 8# was taken from a paper mill in Guangzhou, China. Old book paper (OBP) was gathered from a paper mill in Ningxia, China. Mixed office wastepaper (MOW) used in this study was virgin copy paper which was adhered on the surface by label paper with acrylate-based pressure-sensitive adhesive in order to avoid the interference of ink. The proportion of the label paper in the mixture was 4.5%, and the label paper was adhered to the copy paper for a minimum of 72 hours before pulping (RCA LRP-2). The label paper and copy paper were common commodity grades from

China. The pulp board, which was tested by thermogravimetric analysis (TGA), was market kraft pulp from a paper mill in Guangzhou, China.

### Whitewater and Samples Preparation

OBP, ONP, and MOW (that is, copy paper and label paper), were torn into small pieces (3×3 cm). The paper was then pulped at 60 °C, 300 rpm, and 10% consistency in a Formax 450H High Consistency Repulper (Adirondack Machine, USA). Next, the pulp was diluted to 2%, agitated at 60 °C for 1 hour, and filtrated through a 200-mesh wire screen at 800 rpm in a DDJ-0305 (Cleveland Motion Controls, USA) (Doshi *et al.* 2003a; Castro *et al.* 2004). At last, the filtrate (whitewater with microstickies) was obtained and was used for testing in the subsequent processes (Huo 2002).

Dissolved substances were removed from the whitewater by ultra-filtration membranes with 0.22 µm pore diameter (Doshi *et al.* 2003a). The filter cake (substances retained on the membranes) was dewatered by a BETA 1-8 LD-2 Vacuum Freezing Dryer (Martin Christ, USA) and then used for extraction, TGA, and Py-GC-MS.

### Analytical Methods

#### *Basic properties measurement*

The solids content can be obtained by weighing the samples heated at 105 °C until they are oven-dry. The ash content was obtained after the oven-dry solid substance was carbonized and heated to constant weight in a muffle furnace at 525 ± 25 °C. The extractions of adhesive contaminants were determined following the standard solvent extraction method, by taking dichloromethane (DCM) as solvent (Gruber *et al.* 2000).

The turbidity and cationic demand (CD) of the whitewater were detected with a 2100N Laboratory Turbidimeter (Hach, USA) and with a PCD-04 (Mütek, Germany), respectively.

#### *Thermogravimetric analysis (TGA)*

The samples were placed in a thermogravimetric analyzer TGA Q500 (TA, USA), operating in the temperature range of 25 °C to 700 °C with a heating rate of 20 °C/min under a 40 mL/min flow of N<sub>2</sub>. The results of weight loss rate were collected with TA Instruments Universal Analysis Software.

#### *Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)*

Py-GC-MS was operated in a CDS5150 Series Pyrolyser (CDS, USA) connected to a QP 2010 GC-MS (Shimadzu, Japan). Freeze-dried 0.02 g samples were pyrolyzed at 700 °C for 1 minute. GC qualitative analysis was conducted with a DB-Wax fused silica capillary column (30 m × 0.25 mm, *i.e.*, film thickness 0.25 µm) and the flow rate of He was 1.22 mL/min. The column temperature was held at 50 °C for 5 minutes, and then raised to 280 °C at the rate of 10 °C/min. The injector temperature was 250 °C. The EI-MS scan range was 45 to 600 amu, and the scan time was 0.5 s with the EI ionization energy set at 70 eV.

#### *Quantitative measurement of microstickies*

The size and numbers of microstickies particles and non-stickies particles in whitewater can be measured by a laser particle analyzer, which was based on the FCM technology, and was improved in our lab. In this method, the whitewater was filtered through a diameter of 100 µm screen firstly, which was used to remove large particles to

protect the detector from blocking, and get the fines suspension consisting of microstickies for testing (Vähäsalo *et al.* 2003). Then a kind of sticky control reagent (REF: 05-6100-01, Partec GmbH, Germany), hydrophobic and fluorescent dye, was added into the filtrate. After 5 minutes standing, the microstickies particles were selectively dyed while the non-stickies components in the filtrate were not (Koppinen, 2007). Next, the dyed filtrate was tested and all of these particles were detected when they passed through a transparent tube illuminated by a focused light issued from a 488 nm laser lamp. The information of all particles in whitewater can be obtained via analyzing the signals of the forward scatter (FSC) and side scatter (SSC) lights. At the same time, the fluorescence information of dyed particles, adhesive substances, was picked out and was recorded. These collected signals were compared with the data of standard model microballoons. Then, the quantitative results of all particles and microstickies can be calculated, and the size distribution of particles can be obtained.

## RESULTS AND DISCUSSION

### Basic Properties of Whitewater

The measurement values of the basic physicochemical properties of whitewater from different recovered papers are shown in Table 1. Here, ash content and extraction content were a mass percent of the oven-dry solid substance.

**Table 1.** Physicochemical Properties of Different Kinds of Whitewater

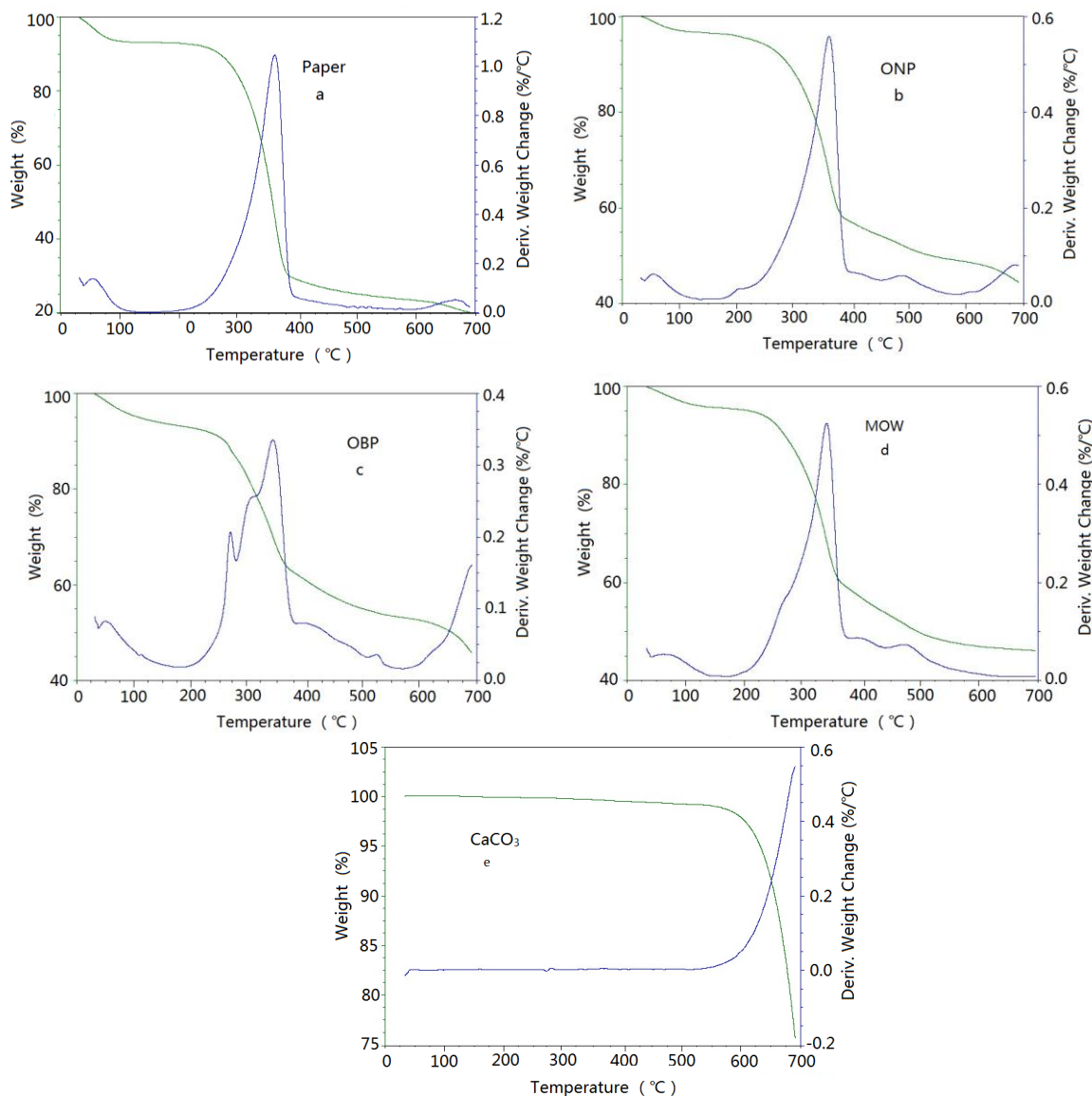
Source	Solid content (%)	Ash (%)	Extraction Content (%)	pH Value	Turbidity (NTU)	CD (-mEq/L)
ONP	0.33	42.73	1.42	7.30	2419	1.15
OBP	0.28	54.93	4.82	7.96	2830	1.04
MOW	0.30	49.15	2.85	8.14	2136	0.75

From Table 1, it can be found that OBP whitewater contained the minimum solid substances, but had the highest ash and extraction content. Conversely, the greatest solids content and the least ash and extraction content were obtained from ONP whitewater. This means that there were more particulates in OBP than in ONP or MOW, while the amount of organic matter originating from the adhesive in OBP was greater than that observed in the case of the other two kinds of paper. The reason might be that there was a large amount of fillers used in OBP to improve the opacity, and the amount of the hot-melt adhesive (HMA) taken as the adhesion agent in OBP was also large. However, fillers usually are not added to the newspaper.

The turbidity values of OBP whitewater were the greatest, while its CD value was in the middle of the three kinds of whitewaters. Alternatively, the maximum CD value and highest turbidity value were measured in ONP's whitewater. Both CD and turbidity values were the lowest in MOW whitewater. That means there were many small particles present in these whitewaters and the number, the distribution, and the charges of these small particles from different kinds of waste papers were also different. However, this information can only roughly reflect the simple characteristics of these small particles and cannot display the accurate size and distribution of these particles.

## TGA of Microstickies

The results of TGA can be used for analyzing the basic features of the organic components and calculating the amount of synthetic polymers, such as stickies (Castro *et al.* 2001) in wastepaper.



**Fig. 1.** TGA and DTG curves of microstickies in different whitewaters

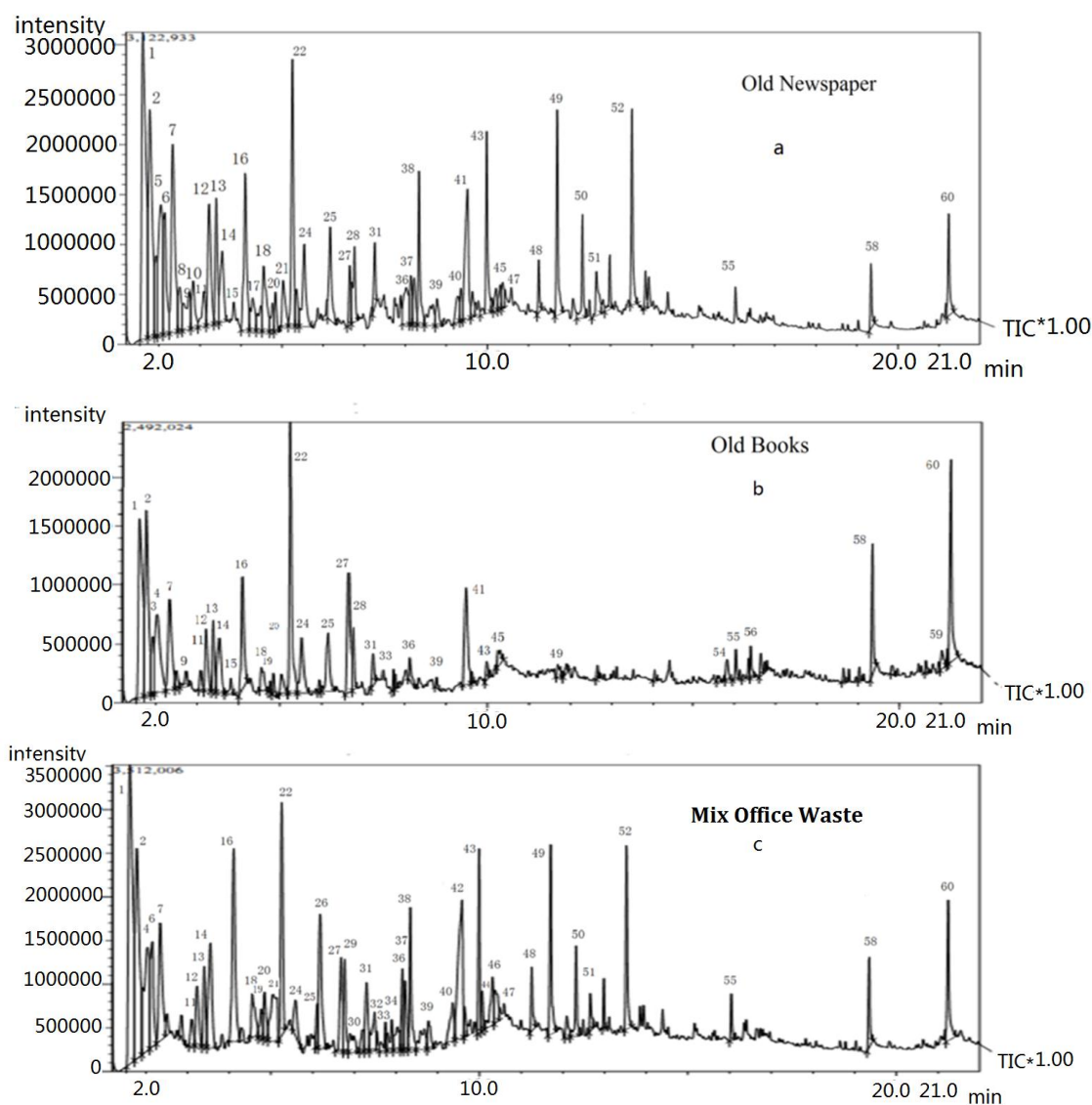
It is shown in Fig. 1(a) that the pyrolysis temperature of the pulp board in a nitrogen atmosphere was in the range of 300 °C to 400 °C, which was consistent with the results of the wood fibers (Castro *et al.* 2001; Guo and Douek 1995). In Fig. 1(b), (c), and (d), the thermogravimetric curves of ONP, OBP, and MOW were similar to the curve of pulp board, but with a wider pyrolysis temperature range compared with the pure fibers shown in Fig. 1(a). The reason might be that the adhesive substances in the three kinds of whitewaters consisted of many synthetic polymers that would decompose in the temperature range between 200 °C and 500 °C.

It can also be seen from Fig. 1(b) and (c) that there was another weight loss from 600 °C to 700 °C. Many stickies contain inorganic constituents (Miranda *et al.* 2008)

such as calcium carbonate ( $\text{CaCO}_3$ , the common inorganic filler used in papermaking of book paper). Compared to the curve in Fig. 1(e), which showed that the  $\text{CaCO}_3$  began to decompose into calcium oxide ( $\text{CaO}$ ) and carbon dioxide ( $\text{CO}_2$ ) at  $600^\circ\text{C}$  to  $700^\circ\text{C}$ , the weight loss at  $600^\circ\text{C}$  in the three figures may stem from the inorganic substances decomposing. In Fig. 1(b) and (c), the inorganic components should originate from fillers. The significant weight reduction at  $650^\circ\text{C}$  in Fig. 1(c) and the smaller weight loss at the same temperature in Fig. 1(b) indicated more filler content in OBP's stickies and less in ONP's stickies, which is consistent with the results in Table 1.

### Py-GC-MS of Microstickies

The filter cakes of the three different kinds of wastepaper were tested by Py-GC-MS, which is an efficient method applied to quantify the classical pyrolytic compounds of stickies (Holmbom 1997; Kanto *et al.* 2005).



**Fig. 2.** Py-GC/MS chromatography of microstickies in different whitewaters

Since the stickies that exist in wastepaper are a very complex mixture consisting of many of the synthetic polymers, it is hard to identify them by conventional methods, such as FTIR and the solvent extraction method (Odermatt *et al.* 2005a,b). The operation temperature of pyrolyzer was chosen as 700 °C, because most stickies have completely decomposed at 700 °C (Fig. 1).

**Table 2.** Pyrolysate from Different Microstickies at 700 °C

No.	Time	Formula	Name	Area %			Possible sources or applications
				ONP	OBP	MOW	
1	1.600	CO <sub>2</sub>	Carbon oxide	10.48	10.78	10.71	Filler, organism pyrolysis
2	1.767	C <sub>4</sub> H <sub>6</sub> O	2-butanone	7.37	9.17	7.42	Coating, solvent of adhesives
3	1.917	C <sub>4</sub> H <sub>11</sub> N	Di-n-butylamine	1.70	2.17		Emulsifier, pesticides, rubber products, dye
4	2.042	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	Diacetyl	-	6.05	4.79	Unsaturated polyester resin, printing ink, paper fertilizer, plasticizers
5	2.050	C <sub>5</sub> H <sub>10</sub> O	2-pentanone	4.51	-	-	Solvent, rubber cement, organic synthetic raw material,
6	2.158	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acetic acid	3.10	-	2.96	Acetic ester, EVA (ethylene vinyl acetate)
7	2.325	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	acetone alcohol	5.73	4.92	3.53	Adhesive aids; pyrolysis product
8	2.508	C <sub>7</sub> H <sub>14</sub>	2-ethyl -3-methylbutylenc	1.17	-	-	Polybutylene base gum
9	2.733	C <sub>6</sub> H <sub>15</sub> NO	N,N-diethyl-2-aminoethanol	1.68	0.70	-	Emulsifier, solvent, corrosion inhibitors, rubber accelerator,
10	2.833	C <sub>7</sub> H <sub>14</sub>	3-methyl-3-hexene	1.33	-	-	Polyethylene comonomer
11	3.092	C <sub>5</sub> H <sub>6</sub> O	1,4-diene-3- ketone	1.02	0.68	0.67	Adhesive, plasticizer
12	3.200	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	1-Isopropoxyacetone	3.20	2.57	1.56	
13	3.375	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	Methyl Pyruvate	2.34	2.35	1.63	Raw materials and intermediates
14	3.550	C <sub>7</sub> H <sub>8</sub>	Spiro[2.4]hepta-4,6-diene	2.12	2.94	3.14	
15	3.817	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	3- furfural	-	0.63	-	Hemicellulose /furfural resin
16	4.092	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	furfural	3.84	4.23	4.95	Hemicellulose, furfural resin
17	4.258	C <sub>8</sub> H <sub>16</sub> O	3,4 -dimethyl -2- hexanone	1.15	-	-	Organic solvent (adhesive)
18	4.533	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	4- cyclopentene -1,3- diketone	2.03	1.16	1.38	Polyacrylate; PEA
19	4.767	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	2- cyclopentene -1,4 diketone	0.66	0.31	0.75	Polyacrylate; PEA
20	4.825	C <sub>6</sub> H <sub>10</sub>	phenylethane	0.71	0.66	1.08	
21	5.008	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	2(5H)- furanone	1.20	0.97	2.58	Furane resins, Hemicellulose
22	5.233	C <sub>8</sub> H <sub>8</sub>	styrene	5.08	9.97	4.29	PS, SIS, SBS, SBR, SDS
23	5.342	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	acetofuran	0.78	-	-	Furan resin adhesive
24	5.533	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	1,2- Cyclopentanedione	2.41	2.84	1.02	Copolymerization accelerator / Resin retarder
25	6.158	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	5- methyl -2- furfural	2.05	3.23	0.68	Furfural resin, Hemicellulose

26	6.175	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	5- methyl -2- furfural	-	-	3.30	Furfural resin, Hemicellulose
27	6.675	C <sub>6</sub> H <sub>7</sub> O <sub>4</sub> P	4-hydroxy-Phenylphosphonic acid	1.57	1.57	2.12	Heat stabilizers and aging agent
28	6.683	C <sub>8</sub> H <sub>17</sub> NO	2,2-diethyl-3-methyl-oxazolidine	1.04	4.83	-	PISOX, reactive diluent used in coatings, water remover
29	6.750	C <sub>9</sub> H <sub>10</sub>	α-vinyltoluene	-	-	1.50	Poly styrene
30	6.892	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub>	7-octenoic acid	-	-	0.85	Ethyl cis-4-octenoate
31	7.233	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	Methyl Cyclopentenolone	1.02	0.98	1.61	Pyrolysate of wood
32	7.483	C <sub>9</sub> H <sub>12</sub>	1H-Indene-,2,3,4,7-tetrachloro	-	-	1.21	Coumatone resin (tackifier) Viscous agent/softener in EVA/PVAc
33	7.742	C <sub>9</sub> H <sub>9</sub> Cl	1H-Indene,1-chloro ,	-	0.44	0.61	Coumatone resin (tackifier)
34	7.892	C <sub>7</sub> H <sub>8</sub> O	2-methylphenol	-	-	0.82	EOCN (o-cresol formaldehyde epoxy resin), ligin
35	8.025	C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>	styrene-2α-dimethyl-acetate	-	-	0.93	Plasticizer, EVA, ABS, PS,
36	8.133	C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	1-methyl-uracil	0.86	0.77	1.38	Pyrolysate of wood
37	8.208	C <sub>7</sub> H <sub>8</sub> O	4- methylphenol	1.00	-	1.40	EOCN
38	8.317	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	guaiacol	2.37	-	2.35	Lignin
39	8.750	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	3 -ethyl -2- hydroxy -2- cyclopentenone	0.66	0.27	0.72	
40	9.350	C <sub>8</sub> H <sub>10</sub> O	xylenol	0.58	-	1.28	Resin, antioxidants, polymerization retarder, dye,
41	9.483	C <sub>6</sub> H <sub>9</sub> NO	4-Methyl-2-oxopentanenitrile	3.76	4.76	-	Coating, adhesive materials
42	9.583	C <sub>6</sub> H <sub>9</sub> NO	4-Methyl-2-oxopentanenitrile	-	-	5.28	Coating, adhesive materials
43	9.958	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	2-Methoxy-5-methylphenol	2.84	0.57	2.30	Lignin
44	10.067	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>	1,4:3,6-Anhydro -α-d-glucopyranose	-	-	0.61	Lignin
45	10.308	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	5-hydroxymethyl-2-furfural	0.51	0.77	-	Fructose-P-cresol resin (adhesive)
46	10.317	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	5-hydroxymethyl-2-furfural	-	-	1.36	Fructose -P-cresol resin
47	10.433	C <sub>8</sub> H <sub>8</sub> O	2,3-Dihydrobenzofuran	0.50	-	0.98	Coumatone resin (tackifier)
48	11.233	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	4-ethyl-2-metoxypheol	0.65	-	0.91	Polymerization retarder, plasticizer, polymer resistance age-resistant
49	11.708	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	4-Hydroxy-3-methylacetophenone	2.98	0.53	2.94	Plasticizer
50	12.300	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	3-Allyl-6-methoxyphenol	1.42	-	1.37	Softwood lignin
51	12.658	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	vanillic aldehyde	1.09	-	0.57	Softwood lignin
52	13.500	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	2- methoxy- -4(1 allyl)phenol	2.72	-	2.65	Softwood lignin
53	13.833	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	6-Methoxy-3-methylbenzofuran	0.52	-	-	Lignin
54	15.825	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	4-hydroxyl-3 methyl-	-	0.82	-	Lignin, pesticides



			phenylacetic acid				
55	16.042	C <sub>15</sub> H <sub>16</sub>	1,3-Diphenylpropane	-	0.79	0.58	BPA (bisphenol A): Epoxy resin, polycarbonate, flame retardants, heat stabilizers, antioxidants,
56	16.350	C <sub>16</sub> H <sub>18</sub>	2,2',5,5'-tetramethyl-1,1'-phenylbenzene	-	0.57	-	Contain benzene adhesive
57	16.400	C <sub>16</sub> H <sub>18</sub>	3,4-diethyl-1,1'-phenylbenzene	-	0.77	-	Solvent
58	19.342	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	pentadecanoic acid	0.81	3.16	1.22	Pyrolysate of wood
59	21.067	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	2,2-bis(4-hydroxyphenyl)propane	-	0.82	-	BPA
60	21.242	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	octadecanoic acid	1.52	6.49	2.47	Stable agent, surfactant of adhesive, lubricant emulsion

It can be seen from Table 2 and Fig. 2 that all three kinds of waste papers contained a large number of different synthetic chemicals. However, the same category of compounds existed in these adhesive contaminants, such as 2-butanone, acetone alcohol, methyl pyruvate, 1,4-diene-3-ketone, 4-hydroxy-phenylphosphonic acid, styrene, furfural, and octadecanoic acid. The presence of those substances in the three kinds of paper can stem from their origination. For example, 2-butanone and acetone alcohol are common organic solvents of adhesives and coatings. 1,4-diene-3-ketene is one kind of plasticizer in HMA and ink binders. 4-hydroxy-phenylphosphonic acid is a normal heat stabilizer and aging agent of adhesives. Styrene is an important co-monomer of styrene-isoprene-styrene (SIS), and styrene butadiene styrene (SBS) and styrene butadiene rubber (SBR) are the basic elastomeric compositions or adhesives used in pressure-sensitive adhesives (PSA) and HMA. At the same time, many latex coatings are copolymers of styrene, and furfural may be the pyrolysis product of furfural resin or hemicelluloses. Octadecanoic acid is widely used as a stabilizing agent, surfactant of adhesive, and lubricant emulsion of paper, so it could be found in all stickies, especially in OBP microstickies. This may be the reason why there is the highest extractives content in ONP, as shown in Table 1. Both ONP and OBP contain oxopentanenitrile, the material of common coating, which means the ONP and OBP are coated, so the filler of coating CaCO<sub>3</sub> appeared in ONP, OBP, and no MOW, as shown in Fig. 1.

In Fig. 2 and Table 2, it can be found that stickies are a complex mixture. The pyrolysate of OBP microstickies contained the most diacetyl, styrene, and 2,2-diethyl-3-methyl-oxazolidine, and other pyrolysis products. They may be byproducts of unsaturated polyester resin, SBR (Lai and Su 2011), PISOX (polyisocyanurate-oxazolidones). Many of them are adhesives or additives (such as heat stabilizers, aging agents stabilizing agent, *etc.*) of HMA used for book binding. The OBP stickies may be only one of the stickies that does not contain EVA (ethylene vinyl acetate). The pyrolysate of MOW microstickies contains acetic acid, 2(5H)-furanone,  $\alpha$ -vinyltoluene, 2-methylphenol, and 1H-Indene-2,3,4,7-tetrachloro, which may originate from EVA, furane resins, poly styrene, EOCN (cresol formaldehyde epoxy resin), and coumarone resin, separately. Since these polymers are usually used as main components for PSA, the pyrolysis products results of the MOW verified this fact. ONP microstickies may contain the most

kinds of adhesive EVA, PEA, SBR, and EOCN (Table 2), which are the same as those contained in the other two pulps. But, polyethylene and 2-pentanone were only detected in the pyrolysis product of ONP sample, which means some components of adhesive were used or existed in ONP stickies. The results have demonstrated that HMA, PSA, coating benders, and wood extractives were the main sources of stickies for ONP, OBP, and MOW, which are the same as those found by Miranda (2008).

From the above, the composition and the origin of stickies in waste paper was complicated, which will result in the difference of stickies characteristics and different effects. Therefore, it is necessary to determine the main composition of the stickies firstly. And then, targeted approaches can be carried out to resolve microstickies problems, such as agglomeration and deposit *etc.*

### Distribution of Particle Size of Microstickies

The results of numbers and size of microstickies in whitewaters are shown in Table 2 and Fig. 3.

**Table 3.** Number and Volume of Microstickies in Whitewaters

Source	Total particle volume (mm <sup>3</sup> /mL)	Micro-stickies volume (mm <sup>3</sup> /mL)	Micro-stickies volume percent (%)	Total particle number (/mL)	Micro-stickies number (/mL)	Micro-stickies number percent (%)	Micro-stickies average diameter (μm)
ONP	15.58	13.17	84.54	48621000	43838000	90.16	8.31
OBP	17.34	15.34	88.08	38107000	28359500	74.42	10.11
MOW	31.63	21.94	69.38	9779500	8337000	85.25	17.13

From Table 3, it can be seen that the volume of total particles in the three kinds of whitewater ranged from 15.58 mm<sup>3</sup>/mL to 31.63 mm<sup>3</sup>/mL, while the volume ranges of microstickies in these whitewaters were 13.17 to 21.94 mm<sup>3</sup>/mL. The volume percentage of microstickies can also be calculated. The largest value of volume percentage of microstickies was 88.47% of OBP whitewater, while the smallest value was 69.36% in the MOW whitewater. In the same way, the number percentage of microstickies against the total particles numbers can also be obtained. The number percentage value of ONP was the highest, the MOW's value was second, and the value of OBP was the least. Using the information obtained about the size and numbers of microstickies, the average diameter of microstickies in whitewater can be deduced. The average particles size were 8.31 μm from the ONP whitewater, 10.11 μm in the whitewater of OBP, and 17.13 μm from the ONP whitewater. This might reflect the characteristics of the adhesives used in different kinds of papers. The particle size of microstickies from HMA was smaller than PSA, but larger than the size of ONP microstickies.

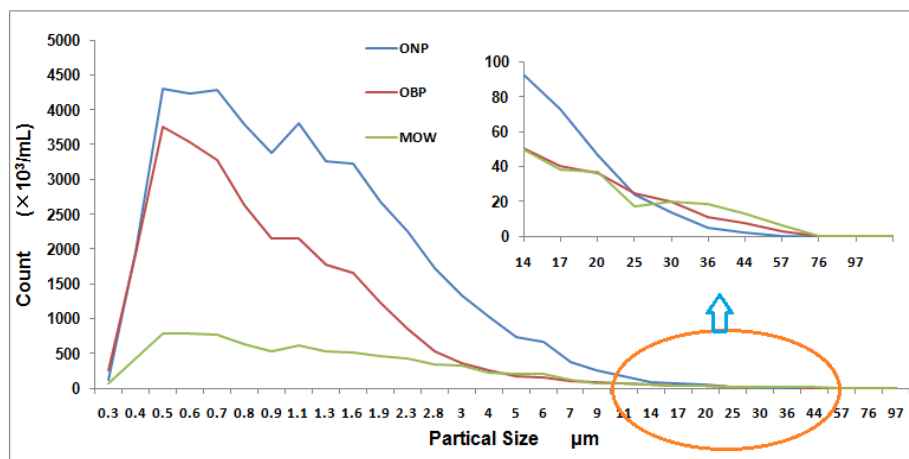


Fig. 3. Particle size distributions of microstickies in different whitewater

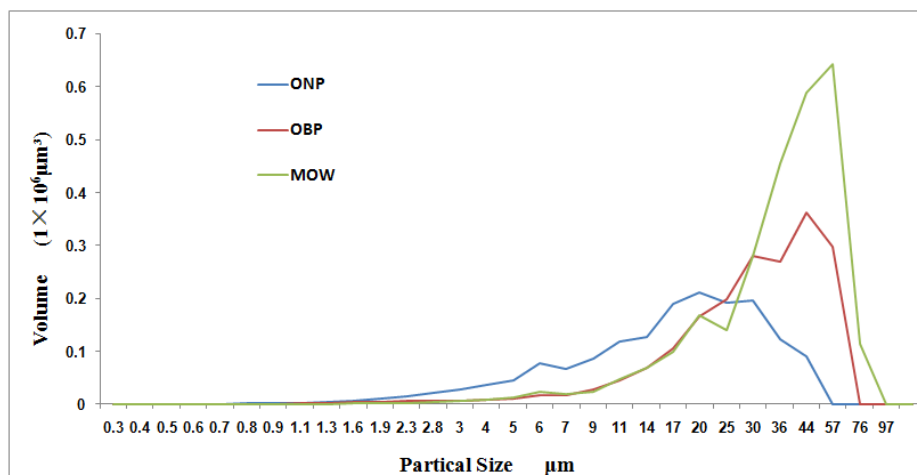


Fig. 4. Volume distributions of microstickies in different whitewater

In Fig. 3 and 4, more details of the number and size of microstickies can be found. Though the diameter of most microstickies ranged from 0.3 to 10  $\mu\text{m}$ , it was clear that the particle size distribution was quite different among microstickies from different kinds of whitewater. The microstickies from MOW had the lowest number: about one-fifth that of ONP, but the total volume of stickies from MOW was almost twice that of ONP (Table 3). The reason might be that the microstickies from MOW mainly contain PSA, which consists of EVA, furfural resin, SIS, and SBS. And all of these components provide elasticity for PSA. Since the main component of PSA exhibited strong viscosity, its microstickies particles were easy to flocculate and precipitate at the lower temperatures. Therefore, the microstickies particles in MOW whitewater had the larger average particle size than the particles size in ONP and OBP whitewater (Table 3, Fig. 3). In addition, the characteristics of the smallest average particle size and other information of OBP whitewater, which can be seen in Table 3 and Fig. 3, may lead to the largest turbidity, as shown in Table 1.

In short, with the results shown in Table 3, Fig. 3, and Fig. 4, more details about the microstickies particles in a certain kind of wastepaper can be reflected and some of the characteristics of microstickies tested by conventional ways can be used to illustrate the quantitative size information further. However, one cannot effectively deduce the size

distribution of microstickies if one relies only on information about the basic features of whitewater and physicochemical properties of microstickies.

## CONCLUSIONS

This study investigated the physicochemical properties of microstickies in whitewater by conventional methods and investigated their size distributions via a laser particle analyzer, which was modified on the basis of FCM. Conclusions can be drawn as follows.

1. Microstickies in whitewater from a certain kind of waste paper would display specific characteristics, which was the difference from those microstickies characteristics in other kinds of waste paper.
  - (1) The ONP microstickies which originated from HMA, PSA, ink, and coating binders, *etc.*: These contained the lowest ash content, the higher turbidity, and the highest CD values, while their volume percentage was in the middle, and it had the minimum average particle diameter. The mean values of particle size were about 8.31  $\mu\text{m}$ .
  - (2) The OBP microstickies, which mainly came from HMA originated from SBR and diacetyl copolymer: The ash content and turbidity reached the highest level, and the CD values were mid-level. The volumes content of microstickies was the highest and the average particle size, 10.11  $\mu\text{m}$ , fell in between the two other kinds of papers.
  - (3) The microstickies in MOW which came from PSA contained EVA, furfural resin, and copolymers of styrene. These microstickies displayed low turbidity and CD values and had the least volumes percent and the largest average particle size. The average size of its particles reached 17.13  $\mu\text{m}$ .
2. With the quantitative size information, the ordinary physicochemical characteristics of whitewater microstickies can be better explained. Meanwhile, the features of size distribution of microstickies can also be illustrated by these characteristics conducted via conventional methods.

To sum up, microstickies in different kinds of waste paper display significantly different characteristics and particle size. This is a premise for analyzing stickies problems. Moreover, in a certain kind of waste paper, the physicochemical properties and the direct determination of size and number of microstickies particle in whitewater can be combined together and taken as a whole to account for more phenomena or deduce more mechanisms, such as stickies agglomeration and deposition, *etc.*

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