Determination of Microstickies in Recycled Whitewater by Headspace Gas Chromatography

X.-S. Chai, J.C. Samp, Q.F. Yang, H.N. Song and J.Y. Zhu

ABSTRACT

This study proposed a novel headspace gas chromatographic (HS-GC) method for determination of adhesive contaminants (microstickies) in recycled whitewater, a fiber containing process stream, in the paper mill. It is based on the adsorption behavior of toluene (as a tracer) on the hydrophobic surface of microstickies, which affects the apparent vapor-liquid equilibration partitioning of toluene. It was found that the equilibrium concentration of toluene in the vapor phase is inversely proportional to the apparent effective surface area of microstickies that remain in the corresponding solution. Thus, the amount of microsticky materials in the recycled whitewater can be quantified by HS-GC via indirect measurement of the toluene content in the vapor phase of the sample without any pretreatment. The presented method is simple, rapid and automated.

KEYWORDS

Adhesives, Adsorption, Gas chromatography, Headspace, Microstickies, Papermaking, Recycling, Stickies, Toluene, VLE, Whitewater.

INTRODUCTION

With the increased use of recycled paper, the removal and control of adhesive contaminants (stickies) becomes a more important issue as these adhesive materials, synthetic polymers, can seriously affect not only the paper quality but also the paper machine runnability during papermaking process [1]. Microstickies, defined as adhesive material able to pass through a laboratory-screening device with 0.006" slots, are unpredictable contaminants. They are relatively benign as long as they stay in colloidal form, but they can agglomerate to form macrostickies at mill process conditions. The accumulation of microstickies in the whitewater may cause the stickies to eventually precipitate from the suspension and cause a deposition problem on the machine, which may lead to paper web breaks and impart holes or spots to the paper sheet [2-3]. The threshold for agglomeration is mill-specific and depends upon the paper produced, the process, and the chemistries employed.

The paper industry has long sought an analytical method that can measure the microstickies' levels in the process whitewater so that preventive action could be taken if their levels were to rise. The analytical methods proposed to date for macrostickies measurement have usually involved deposition on a surface or a wire, but these tests are too time-consuming to be useful for the process applications. Other methods use solvent extraction, which will also detect other extraneous material and will not always dissolve the critical synthetic polymers. All these methods have been summarized and reviewed in the literature [4].

The IPST method, the only technique for microsticky measurement, has been recently proposed [5]. It was based on measuring the total organic carbon (TOC) content of a sample filtered through a 3,000–10,000 Dalton cut-off membrane, in which it assumes that the high molecular weight (MW) compounds within this range are the microstickies. A typical preparation of the sample fraction for TOC measurement in IPST method [5] is illustrated in Figure 1.

Obviously, the MW cut-off margins in this approach are empirical, and the materials other than stickies (e.g., starch) that all have high MW in process stream will also be collected in this way and contribute to TOC counts as the sticky materials in this method. Therefore, the results from the IPST method do not accurately represent the amount of microstickies in process stream, and will provide a poor correlation to the paper-machine runnability in many cases, especially for the process stream with a significant amount of starch.

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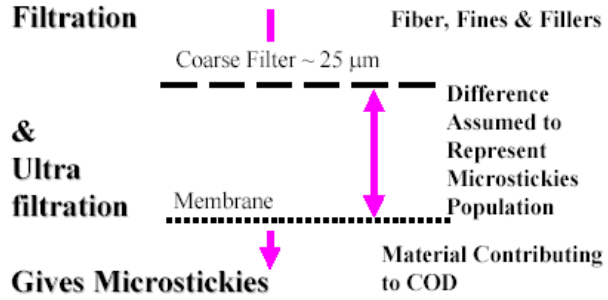

Figure 1. **Sample preparation in the TOC based micro-stickie measurement method [5].**

Headspace gas chromatography (HS-GC) is a powerful technique for analysis of volatile species in the samples having a complicated matrix. The headspace technique also provides the opportunities for conducting sample pretreatment and conditioning during the testing, e.g., to convert non-volatile species to volatile ones that can be analyzed by GC [6-8], and sample heating and shaking. Recently, we have developed an HS-GC technique for measuring solubility of inorganic salts in aqueous solution, using methanol as a tracer [9], based on a salting effect on the methanol vapor-liquid equilibrium (VLE) behavior observed previously [10]. It is known that the problem caused by the microstickies is due to their hydrophobic surface property of sticky particles in aqueous systems. We believe that the surface hydrophobic property of stickies can affect the VLE behavior of toluene, thus a correlation between the amount of stickies in the liquid sample and content of toluene in the vapor phase can be built.

The objective of this study was to develop a novel HS-GC method that can determine microstickies in the recycled whitewater. The effects of other major coexisting materials in the process stream were also evaluated.

EXPERIMENTAL

Materials

Four commercial brands (i.e., Carbtec, Avery acrylic, HYCAR 26288 and PAS) of sticky polymers commonly used in paper related products were received from mills. The polymers are mainly polyacrylates such as polymethylmethacrylate (PMMA) and their copolymers, and hot melts, e.g., polyvinyl acetate (PVAc). However, the exact compositions in these samples are confidential. The average particle sizes of these polymers are around 0.7µm.

Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph equipped with a flame ionization detector (FID) (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA.). GC conditions were: capillary column (HP-5, Agilent Technologies) with an ID = 0.32 mm, film thickness of 0.25 µm, and a length of 30 m at a constant temperature (30°C), helium carrier gas flow rate of 3.1 mL/min. The GC running time is 4 minutes. Headspace Sampler operating conditions were: oven temperature of 32°C; 10 min strong shaking of the sample; vial pressurized by helium and pressurization time of 0.2 min; sample-loop fill time of 0.2 min; loop equilibration time of 0.05 min; vial equilibration time of 0.5 min; and loop fill time of 1.0 min.

A custom built compressed air cooling conduit was introduced into the sampler system, in which the cooling conduit is inserted directly into the oven (from the ceiling). By continuingly blowing the compressed air, it can bring the temperature down to 32°C.

The sample preparation and measurement procedures were as follows: 5 mL sample solution was added into a 20 mL headspace testing vial (Agilent Technologies) and sealed by septum. Then, a 10 µL of standard toluene-methanol solution (85 ppm toluene, on volume/volume basis) was injected into the vial that contains 5 mL sample solution, thus the toluene concentration in the tested sample solution is 170 ppb. The vial was placed in the headspace sampler tray for automatic HS-GC measurements.

Particle size distributions were measured with a Malvern Zetasizer 3000 (Malvern Instruments Ltd, Malvern, UK) based on a quasi-elastic light scattering technique. The sample solution is placed in a 250 mL beaker for particle size measurement, the sample dilution may be required if the amount of microstickies is high.

RESULTS AND DISCUSSIONS

Principle

The VLE partitioning coefficient for a volatile organic solute in an aqueous solution is defined as,

$$K = \frac{C_g}{C_l} \qquad (1)$$

All symbols are defined in Table 1.

The VLE partitioning coefficient is constant, i.e., agrees with Henry's Law, if the concentration of the solute is very low, in which the molecular interactions between solutes themselves are negligible. When the aqueous solution system contains solid phase (particle substances) that have the hydrophobic surface, it can adsorb hydrophobic solutes, such as toluene. As a result, the solutes are partitioned

Table 1. **Symbols and definitions**

K	vapor-liquid equilibrium partitioning coefficient
C_g	concentration of the solute in vapor phase
C_l	concentration of the solute in liquid phase
C_l^0	initial concentration of solute in the solution
C_s	concentration of the solute adsorbed by the adhesive substance in the solution
k_1	adsorptivity of the solute on the polymer substances.
C_s	concentration absorbed in solid phase
A	GC peak area
k_2	GC response factor
S	apparent effective surface area
X_s	amount of microstickies
d	average diameter of microsticky particles
k_v	ratio factor of volume-to-mass of sticky material
k	hydrophobic characterization coefficient of the polymers
a	Intercept
b	slope

between both vapor-liquid and liquid-solid phases. With the presence of hydrophobic solid phase, the solute concentration in liquid phase can be written as,

$$C_l = C_l^0 - C_s \tag{2}$$

According to Eqns. (1) and (2), the relationship between the solute concentrations in vapor phase and in solid phase at the equilibrium can be expressed as,

$$C_g = K(C_l^0 - C_s) \tag{3}$$

For a given amount of solute, its concentration absorbed in solid phase, C_s, is proportional to the apparent effective surface area, i.e.,

$$C_s = k_1 S \tag{4}$$

According to Eqns. (3) and (4), we can build up a relationship between C_g and S, that is,

$$C_g = KC_l^0 - Kk_1 S \tag{5}$$

Since GC peak area is proportional to the solute concentration in the vapor phase, i.e.,

$$C_g = k_2 A \tag{6}$$

we can build up the relationship between the GC signal and apparent effective surface area of polymer substances, i.e.,

$$A = \frac{1}{k_2}\left(KC_l^0 - Kk_1 S\right) = a - K_2 S \tag{7}$$

where both intercept (a) and slope (K_2) are constants, which can be obtained through calibration.

Since the relationship of the apparent effective surface and the amount of sticky particles can be written as,

$$S = kk_v \frac{X_s}{d} \tag{8}$$

according to Eqns. (7) and (8), we can obtain

$$A = a - K_2 kk_v \frac{X_s}{d} = a - bX_s \tag{9}$$

Therefore, if the particle size information is available, the amount of polymer substances can be quantified based on headspace GC method using a volatile organic compound species as the tracer.

Microstickie particle size distribution in the recycled whitewater.

In a previous work [11], the particle size distribution of microstickies in the simulated recycled whitewater was investigated. Similar to the industrial process, the recycled paper needs to be dispersed in the aqueous medium to release the fibers, it can be achieved in a high-speed homogenizer. However, this process also generates microstickies from the macrostickies. In this work, the suspension of microstickies was generated based on the dried adhesive polymer through a high-speed homogenizer. It was found that the particle size generated by this way is below 4 mm, in which the most portions of particles are located around the size of 0.7 mm.

Tracer and its concentration introduced in the testing solution

In this work, toluene was chosen as a tracer because it has not only a reasonable hydrophobicity and solubility in water, but also a shorter retention time (3.1 minutes) in the GC measurement.

As reported [11], the amounts of microstickies in paper mill recycling stream after passing through 0.006" slots are varied from 100 to 1000 ppm. Therefore, the proper tracer concentration introduced into the tested solution is important to achieve relatively large decreases in the vapor toluene concentration. Although higher toluene concentration should lead to higher GC signal, it is more difficult to see small changes in the amount of toluene adsorbed if the total toluene concentration is very high. According to Eqn. (2), if the initial concentration (C_l^0) of tracer in the testing solution is too high, the portion of

toluene adsorbed by sticky particle will be relatively low. Thus, it leads to a lower detecting sensitivity on the microstickies measurement as shown in Figure 2. On the other hand, a high tracer concentration may also create a multiple layer adsorption on the particle surface, which may result in a non-linear relationship between the vapor content of the tracer in the headspace and amount of the microstickies in the sample. Our experiment showed that a concentration about 170 ppb (in the testing solutions) is proper in the testing. Since 170 ppb is much lower than the solubility of toluene in water at a testing temperature [12], it can be quickly dissolved in the aqueous solution. The standard toluene solution (85 ppm) can be easily prepared by adding a small amount of pure toluene (by microsyringe) into a given volume of pure methanol. In the microstickies testing, a very small volume (10 µl) of the standard toluene-methanol solution is added into the sample solution, in which the concentration of methanol in the testing solution is about 2000 ppm (v/v). Since nature of methanol is very close to that of water, a small amount of methanol in the testing solution does not affect the adsorption behavior of toluene on the sticky substances.

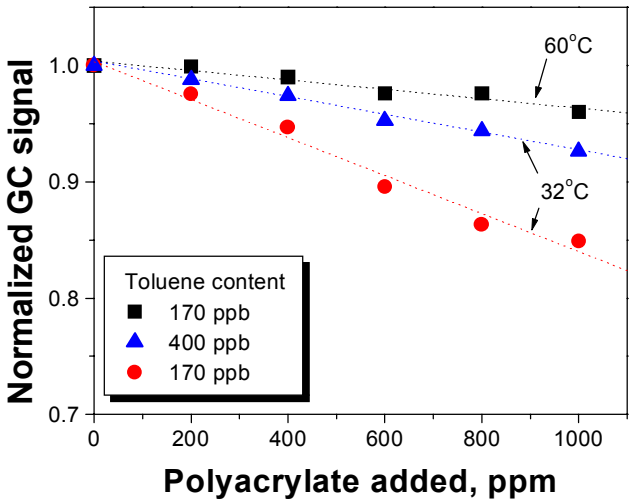

Figure 2. **Temperature effect of toluene adsorption on sticky particles.**

Temperature effect of toluene adsorption equilibrium on microstickies

Due to a lower glass transition point for most sticky polymers, a higher temperature (above 50°C) can easily cause the microstickies agglomeration during the sample VLE, in which the uncertainty of particle size distribution will affect the measurement. As shown in Figure 2, both lower temperature and larger amount of microstickies cause a more significant decreasing in GC signal, which makes the microstickies measurement more sensitive. However, there is no cooling system available in the current headspace sampler (HP-7694), which causes the difficulty to perform an equilibration below ~40°C. Therefore, a custom-designed compressed air-blow cooling system as described above was implemented into the headspace sampler, which can bring the temperature down to 32°C.

Equilibration time for toluene adsorption.

For quantification analysis, it is important to achieve a complete equilibration in the present three-phase "wet" system. It was reported that the equilibration time of volatile organic compounds adsorption/desorption in the "dried" system, e.g., the dried polymers [13] or the packaging materials [14-16], are very long, usually takes hours. However, the equilibrations in the "wet" system, e.g., add a solvent as a displacer to the dried polymer [13] or in a polymer latex [17], are much faster. In this work, we found that the toluene adsorption equilibration on the microstickies in the aqueous system is very fast, which can be achieved within 5 minutes as shown in Figure 3. In the present work, the equilibration time in all testing is 10 minutes.

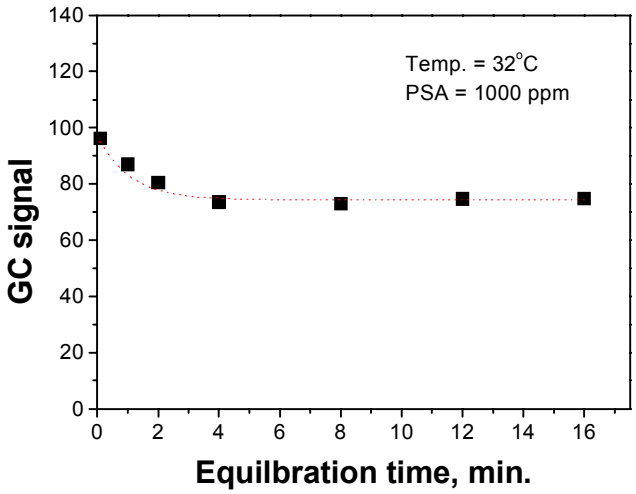

Figure 3. **Equilibration time for the toluene-microstickies aqueous system.**

Headspace GC testing on the commercial microstickies.

Figure 4 shows the results on four sets of microsticky sample solutions with a content level from 0 – 1000 ppm. Although the compositions in these sticky samples are different, they basically fall on the same line, which agrees with Eqn. (9), i.e., the GC signals linearly decrease with the amount of microstickies in the solutions. Thus, the present headspace GC technique can be used for the quantification of the microstickies in the recycled whitewater if there is no significant interference from the coexisting species. Obviously, the present method is much simpler and fast because it avoids the complicated and time consuming procedures such as filtration and ultra-filtration as reported in the previous method [5]. The results also showed that the hydrophobic properties of these sticky polymers commonly used in the paper industry are quite similar, which makes the calibration procedure easier.

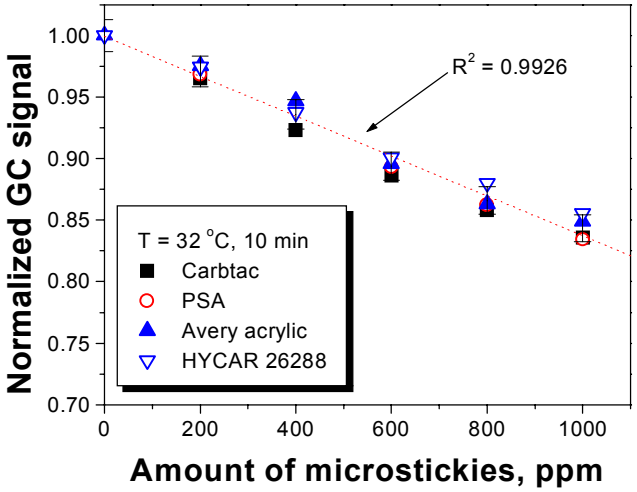

Figure 4. **Relationship between GC signals (normalized) of vapor toluene and the amount of microstickies in the solution.**

It should be pointed out that the agglomeration of microstickies to form macrostickies during the papermaking process is the major cause that affects the paper machine runnability. Such an agglomeration is related to the natures of the sticky materials, mainly their hydrophobicity. Therefore, we believe that the apparent effective surface (*S*) as we defined in Eqn. (8), instead of the amount of the microstickies, is a more proper parameter to evaluate their impact to the process. However, at the present time the paper industry uses the amount of the sticky substances to correlate to their process performance.

Effects of the other coexisting materials

There are many sorts of the suspended substances such as cellulose fines, fillers (e.g., clay) and retention aid agent (typically the cationic starch) remaining in the clarified recycle-whitewater. Therefore, the effect of these coexisted species on the toluene measurement should also be investigated. As shown in Table 2, all these major coexisting suspended species have no significant effect on the toluene VLE behavior; we believe that is probably due to the hydrophilic nature of these substances. In order to confirm this, a water-soluble polymer, polyvinyl alcohol (PVOH) was used in the testing. The results showed that the addition of PVOH dose not affect the toluene VLE behavior. Our testing also showed that there is no significant salting effect on toluene VLE behavior observed at an ionic strength range of 0 - 0.1 mol/L, as met in the recycled whitewater. Since the coexisting species in the recycled whitewater are very diluted; it could be also one of the reasons that their effects on toluene VLE are not significant.

Method precision and method validation

The repeatability of the method was conducted by both using a 10 µL toluene-methanol solution in five vials where containing 5 mL solution with the microstickies content of 600 ppm. The result shows that the average relative standard deviation (RSD) from 5 measurements is less than 7 %.

As mentioned above, the only reported technique (i.e., IPST method [5]) for microstickies task lacks of the fundamental basis to measure the microstickies in the recycle whitewater, and therefore it is not acceptable to be a reference method. In this work, the present method was evaluated by a set of synthetic whitewater (containing a certain amount of fines, clay and starch) with the standard microstickies addition. The samples were then measured by HS-GC. The normalized GC signals (i.e., set the signal for blank testing as one) were used to calculate the content of the microstickies by the following equation, i.e.,

$$A = 0.996(\pm 0.005) - 1.686\times 10^{-4}(\pm 8.4\times 10^{-6})X_s \quad (10)$$

which is based on the data presented in Figure 4.

From Table 3, it can be seen that the data from HS-GC measurement matched those by the standard addition, indicating that the present method is justifiable. The measurement error (~12 %) is acceptable in the paper mill application.

It should be pointed out that the adsorption systems may have only a very narrow linear concentration range [13]. In our previous work, it was observed that a methyl methacrylate VLE relationship in an aqueous solution containing more than 1000-1500 ppm of polymethyl-methacrylate particles is non-linear [18]. Therefore, it is

Table 2. **Effect of the major coexisting species on toluene VLE behaviors.**

Fine		Clay		Starch		NaCl	
Content ppm	GC signal	Content ppm	GC signal	Content ppm	GC signal	Content mol/L	GC signal
0	99.9	0	100.4	0	100.8	0	100.8
200	100.1	40	99.0	200	100.4	0.02	100.4
400	99.9	80	100.9	400	99.5	0.04	99.5
600	98.9	120	100.7	600	101.0	0.06	101
800	99.7	200	101.4	800	100.6	0.08	100.6
1000	98.3	300	99.6	1000	101.4	0.1	101.4

Table 3. **Differences between the known amounts of microstickies added and measured by HE-GC in the synthetic samples.**

Sample	Microstickies (ppm)		Relative difference (%)
	Standard added	HE-GC measured	
1	200	225	12.5
2	400	360	-10.0
3	600	620	3.3
4	800	787	-1.6
5	1000	881	-11.9

suggested that in present method sample be diluted when microstickies content is greater than 1000 ppm.

Remarks

As mentioned above, the apparent effective surface area (*S*) of microstickies, rather than the amount of microstickies, could be a more reasonable parameter that correlates to the microstickies problem in the paper formation process. Clearly, the apparent effective surface area of microstickies is also a function of the process conditions, e.g., temperature. Therefore, further development of the present method is really dependent on the industrial needs and understanding the issue of microstickies to evaluate the microstickies' effect on the process operations [19]. The present method can definitely provide an effective tool for this purpose for both microstickies quantification and characterization studies.

CONCLUSIONS

We have demonstrated a headspace GC technique for the determination of microstickies in white water. The present method can easily determine the amount of microstickies by measuring the vapor tracer content based on headspace GC, which avoids the complicated and time consuming procedures such as filtration, ultra-filtration, and solvent extraction methods. The study shows that the other compositions in the recycled white water such as fibers, fines, filler, inorganic ions, and retention aid agent have no significant interference with the microstickies determination in the present method.

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