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Article

# Surface Modification of Adsorbents for Removing Microstickies from Papermaking Whitewater

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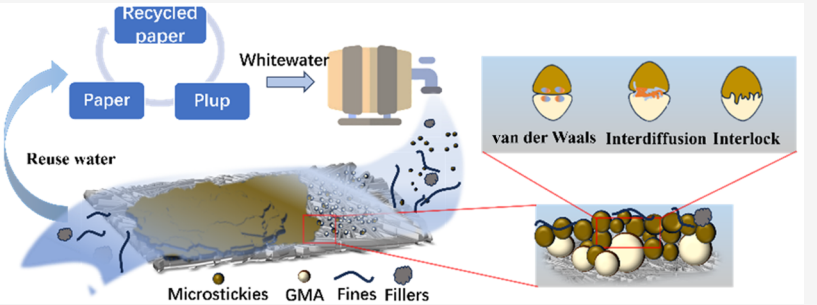


**ABSTRACT:** Adhesion and agglomeration of small sticky particles, i.e., microstickies, onto paper and paper machines cause serious problems for recycling mills. Because associations between materials with similar surface energies are strongest, we propose an "adhesives collect stickies" strategy to physically remove microstickies from whitewater systems. We characterized deposits from a commercial paper machine and observed a large amount of acrylate-based materials. Based on this observation, we chose to graft glycidyl methacrylate (GMA) to surfaces of polypropylene (PP) to make it more similar to the deposited stickies, which will encourage association by van der Waals forces and interdiffusion. The modified material efficiently collected acrylic adhesive particles suspended in water (58.3%) and particles found in paper mill whitewater (40.6%). Additionally, a flow cell incorporating layers of modified mats of fibers shows good efficiency (40.6−49.4%) for collecting stickies at steady flow rates. This strategy may provide a method for removing microstickies without disturbing the chemical environment of the papermaking system.

## 1. INTRODUCTION

Recovered paper is a major raw material for the paper industry. It can provide advantages by reducing energy consumption and lowering environmental impacts.[1] However, recovered paper carries with it various sticky substances, such as pressure sensitive adhesives, hot melt adhesives, and resins. Small particles of these materials, i.e., stickies, tend to accumulate in papermaking whitewater loops, and the adhesive properties of these materials cause them to intermittently deposit on surfaces of equipment. Deposition of stickies can lead to reductions in machine runnability and increases in web breaks, which ultimately reduce economic efficiency.

Due to a wide range of compositions and properties of stickies, developing strategies to remove them from papermaking systems is difficult.[2−4] Proposed methods of stickies control include physical, chemical, and bioenzymatic methods.[5,6] Physical methods currently used in the paper industry include screening, cleaning, and flotation.[7] These methods effectively remove stickies larger than 100 $\mu$m, but there are challenges in removing microstickies (5−100 $\mu$m). Dispersion is commonly used by mills to reduce the size of the stickies. While this method reduces the immediate impact of stickies on production, the dispersed microstickies persist and gradually accumulate in whitewater loops, eventually leading to production issues. Current chemical and bioenzymatic methods primarily encapsulate stickies particles or hydrolyze certain chemical bonds to reduce their size.[8,9] These methods can mitigate the impact of microstickies on mills but do not remove them, so they still accumulate in water loops. There is an urgent need for effective removal of microstickies from whitewater.

Physical adhesion to surfaces of various materials can remove microstickies from whitewater.[10,11] Doshi et al. studied deposition of microstickies surfaces of polypropylene (PP) microfoam, low-density polyethylene film (LDPE), a flat piece of high-density polyethylene (HDPE), and polyester wire.[12] This study indicated both identity and morphology of surfaces affect the deposition rate. Xu et al. studied effects of metal

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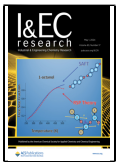

surface roughness on the deposition of whitewater microstickies; the results showed flat surfaces promote aggregation and deposition of microstickies particles.[11] However, it remains unclear how to select and design suitable materials to promote the adhesion of microstickies. In fact, the effectiveness of each design depends on the chemical and physical characteristics of each contaminant.[13] In paper production, aggregation and deposition of stickies cause problems, so providing a location that promotes deposition may reduce deposition in problematic locations. This inspired a strategy of "adhesives collect stickies" where materials are developed that have similar chemical properties to microstickies for collecting them from papermaking whitewater.

We first did compositional analysis of sticky deposits from a mill and then selected a similar adhesive to add to collector surfaces. For the substrate, we chose polypropylene (PP) nonwoven fabric because it is easy to do surface modification and provides good adsorption performance.[14,15] The modified collector was obtained by grafting the selected adhesive onto PP nonwoven fabric through ultraviolet (UV) irradiation. The effectiveness and selectivity of this collector was tested with model stickies suspensions and recycled paper whitewater (hereinafter called "whitewater"). Finally, adhesion experiments at different whitewater flow rates demonstrated the scalability of this strategy.

## 2. MATERIALS AND METHODS

**2.1. Materials.** The deposited stickies and recycled deinked pulp were obtained from the Huatai Group Co. Ltd. (Shandong, China). The PP nonwoven fabric was supplied by JinLv Co. Ltd. Glycidyl methacrylate (GMA, 97% with 100 ppm 4-methoxyphenol stabilizer), copper reagent (sodium diethyldithiocarbamate, polymerization inhibitor), and benzophenone (BP, photosensitizer) were purchased from McLean Co. Ltd. (Shanghai, China). Rosin resin was obtained from Haixin Chemical Co. Ltd. (Henan, China). Waterborne acrylate adhesives and styrene−butadiene latex (SBR, solids 50% ± 1) were purchased from Yoshida Chemical Co. Ltd. (Shenzhen, China). The fluorescence tracer was Nile red, supplied by Partec (Munster, Germany).

**2.2. Experimental Methods.** *2.2.1. Composition Analysis of Stickies.* Stickies deposited on a paper machine were collected and sequentially extracted with ethanol and chloroform using an automatic Soxhlet extractor (Soxtec 2050, FOSS, Sweden). The ethanol extraction process was carried out for 4 h at 250 °C. The chloroform extraction process was carried out for 4 h at 140 °C. The residual components were calcined in a muffle furnace (SX2−2.5−10NP, Yiheng Co. Ltd., China) at 575 °C for 4 h.

*2.2.2. PP-GMA Mat Fabrication.* The PP nonwoven fabric was cut into a rectangle (about 20 × 15 × 0.1 $cm^3$) and then sonicated for 15 min in ethanol to eliminate impurities. The mats were dried in an oven at 60 °C to a constant weight. The grafting solution was prepared by adding 0.2 wt % copper reagent, 0.2 wt % BP, and 5 wt % GMA to 20% ethanol (v/v). The mat and grafting solution were placed in a sealed bag, and the air in the bag was displaced by nitrogen. The fabric was submerged in the grafting solution and allowed to soak for 4 h. The sealed bag was placed under a UV lamp and irradiated at an intensity of 50 mW/$cm^2$ for 5−20 min,[16] and then cooled to room temperature. After grafting, the mats were sonicated for 10 min first in pure water and then in ethanol to remove unreacted monomers, homopolymers, and benzophenones. The mat was then air-dried.

The grafting rate ($G$) to the polypropylene mat was calculated as eq 1

$$G = \frac{W_1 - W_0}{W_0} \times 100\% \tag{1}$$

where $W_0$ is the weight of mat before modification and $W_1$ is the weight of mat after modification and washing.

*2.2.3. Preparation of Model Stickies Suspension and Whitewater.* Rosin resin suspension (0.1 wt %) was prepared by dissolving rosin resin in ethanol and then dispersing it in water. SBR suspension (0.1 wt %) and acrylic adhesive suspension (0.1 wt %) were stable and simply diluted with water and thoroughly mixed. Recycled paper pulp was diluted to 1 wt % with water and agitated at 50 °C and 350 rpm for 1 h. The three types of suspensions and whitewater were filtered through a dynamic drainage jar (DDJ, MT2110−086CF, Cleveland Motion Controls, USA) with a standard net of 200 mesh. The filtrates and dispersed whitewater were collected for use.

*2.2.4. Collector Construction and Adhesion Experiments.* A collector tank was constructed from plexiglass panels with five slots for removable panels. Modified fiber mats were fixed to panels and placed into slots inside the tank. Whitewater was added through the hole at the top of the tank. Slurries flowing over the panels contacted the fiber mats. The optimum flow rate range was 3−15 L/min. When the flow rate was lower than 3 L/min, whitewater did not flow continuously through the device. When the flow rate was >15 L/min, whitewater did not have enough time to make full contact with the mats.

The suspensions and whitewater samples were incubated at 50 °C before the experiments. For static experiments, approximately 1 L of model stickies suspensions (or dispersed whitewater) was added to a single mat. The treated water was collected and analyzed.

**2.3. Characterization.** The chemical groups in samples and effectiveness of the grafting reaction was determined with Fourier transform infrared (FTIR) spectroscopy (TENSOR27, BURKER, Germany). The chemical composition of extracts from deposited stickies was determined by pyrolysis−gas chromatography−mass spectrometry (Py−GC−MS, R7890B-5977A, Agilent, USA). Cracking temperature was 600 °C for 5 min. Chromatographic conditions were as follows: column temperature at 50 °C for 2 min, 5 °C/min; final temperature at 280 °C for 15 min; inlet temperature at 250 °C; carrier gas He, 1 mL/min split ratio of 50:1. Mass spectrometry conditions: E1 ion source; E1 source electron energy 70 eV; ion source temperature 230 °C, quadrupole temperature 150 °C, interface temperature 280 °C; mass scan range 30−550 $m/z$. Peak identification was accomplished by comparison with a NIST (National Institute of Standards and Technology) 2008 library.

The morphology of deposited stickies, PP and PP-GMA mats were characterized using a scanning electron microscope (SEM, SU5000, Hitachi, Japan). The contact angle of the samples was tested by a contact angle meter (OCA 40, Data Physics, Germany). The turbidity of the whitewater before and after adhesion was measured by a turbidimeter (2100N, HACH, USA).

**2.4. Quantitative Measurement and Analysis of Microstickies in Whitewater.** The residual microstickies in whitewater were determined by a particle-sorting microfluidic



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pulse spectrophotometer system, which was previously described.[17,18] The system consists of fluid pumps, an all-solid-state sapphire laser (SAPPHIRE 488−20, COHERENT, Germany) with an output wavelength of 488 nm and an output power of 20 mW, and signal analysis systems. The particles require staining to be efficiently detected. For sample preparation, 10 $\mu$L of fluorescent tracer solution, 10 $\mu$L of whitewater, and 100 $\mu$L of ultrapure water were mixed. The sample was allowed to stand in the dark for 5 min to ensure full contact between the fluorescent tracer and stickies. Finally, the sample was diluted to 1 mL with ultrapure water for testing. The diluted sample was pumped through a glass tube illuminated with a laser. The size and number of particles were optically detected in both the forward and transverse directions. The stained sticks emitted 635 nm light under 488 nm laser excitation. The number and size distribution of microstickies was determined using information obtained from forward and transverse fluorescence detectors. The schematic of the particle-sorting microfluidic pulse spectrophotometer system is shown in Figure 1.

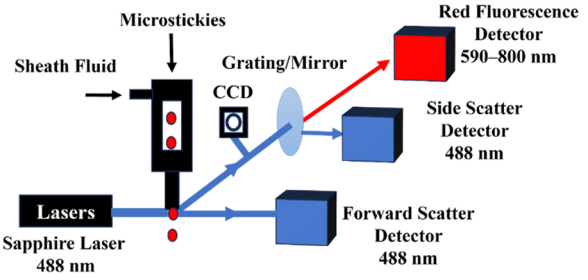


**Figure 1.** Schematic of the particle-sorting microfluidic pulsed spectrophotometer system.

The removal effect of whitewater microstickies was primarily expressed by the volume change of the microstickies. The adhesion efficiency ($\eta$) was expressed by eq 2:

$$\eta = \frac{v_0 - v_1}{v_0} \times 100\% \tag{2}$$

where $v_0$ is the total volume before and $v_1$ is the total volume of particles after the treatment.

The size distribution of microstickies was characterized in terms of the number frequency ($f_n$) and the volume frequency ($f_v$), which were calculated as follows:

$$f_n = \frac{n_i}{n} \times 100\% \tag{3}$$

$$f_v = \frac{v_i}{v} \times 100\% \tag{4}$$

where $n$ and $v$ refer to the total number of particles and the total volume. $n_i$ and $v_i$ ($i$ = 1, 2, 3, ...) refer to the total number and volume of particles in a given diameter range.

## 3. RESULTS AND DISCUSSION

**3.1. Composition Analysis of Deposited Stickies.** Stickies deposits can be found at different locations on papermaking equipment. They are complex mixtures that include a variety of adhesive components, fiber fines, and papermaking fillers. The #2 drying cylinder was located at the start of the drying section, and the #36 drying cylinder was located at the end of the drying section. As shown in Figure 2a, the #2 deposited stickies were black flakes with a powdery grayish-white substance attached to one side. The powdery substances mainly consisted of fiber fines and fillers. The #36 deposited stickies are more homogeneous and consisted of a black polymeric material (Figure 2b). To further analyze their

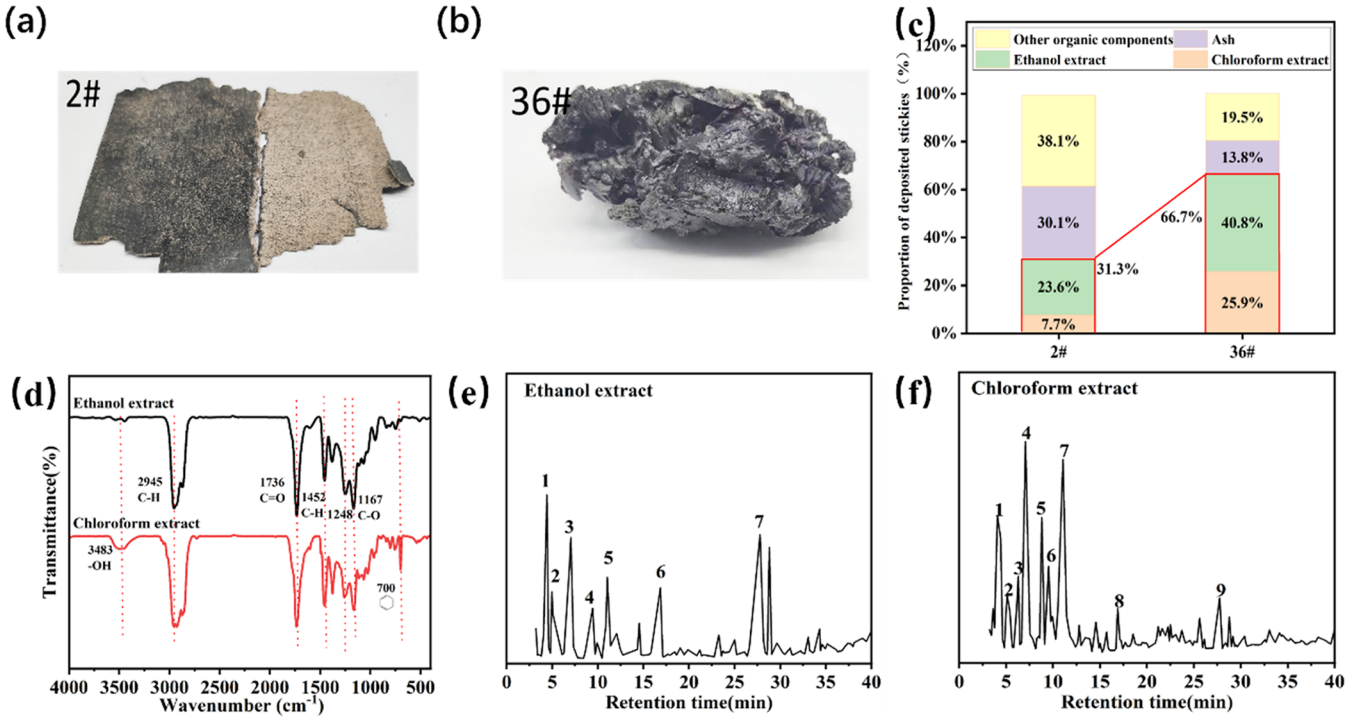


**Figure 2.** Images of (a) #2 and (b) #36 deposited stickies. (c) Proportion of deposited stickies, (d) FTIR spectrum, (e) Py-GC-MS chromatograms of ethanol extract, and (f) Py-GC-MS chromatograms of chloroform extract.



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compositions, the deposited stickies were sequentially extracted with ethanol and chloroform,[19] followed by ash determination on the residue. As shown in Figure 2c, solvent extracts accounted for 31.3 and 66.7 wt % of the #2 and #36 deposited stickies, respectively. Therefore, the deposited stickies contained numerous components some of which were not soluble in ethanol or chloroform yet were lost during ash determination. These unidentified substances were called other organic fraction (Figure 2c).[19]

These results demonstrate that adhesive components were more likely to adhere to nonadhesive substances at the beginning of the drying section. At the end of the drying section, adhesive components were more likely to adhere to other adhesive components. This phenomenon is likely associated with the strength and moisture content of the paper web. When the paper began to dry, microstickies were destabilized and deposited on the drying cylinder. Initially, fibers of the web did not form a stable bonding network. Therefore, fibers, fines, and inorganic fillers in the paper web are carried with the stickies. At the end of the dryers, stickies in the paper web were still adhered to the surface of the drying cylinder, but it is difficult to pull the fines and fillers from the paper web. These results indicate that the strength of bonding formed between the adhesive is likely high and that deposition of stickies was the result of the aggregation of many adhesive components.

The chemical compositions in the solvent extract from the 2# deposited stickies was analyzed by FTIR and Py-GC-MS. In the FTIR spectrum of the ethanol extract (Figure 2d), the strong absorption peak at 1736 $cm^{-1}$ was due to C═O stretching of the acetate group. The bands at 1248 and 1167 $cm^{-1}$ were due to C−O stretching of the ester group.[20] It can be inferred that the ethanol extract contained esters.[19] Figure 2e shows the Py-GC-MS chromatogram of the ethanol extract, and the major components are shown in Table 1. The analysis reveals that the main components among the cleavage products are alkanes and polyesters. In addition, the 2-ethylhexan-1-ol is a cleavage product of 2-ethylhexyl acrylate in the Py-GC-MS test. Therefore, it was not originally present in the ethanol extract. These results indicate the presence of a significant quantity of polyacrylate polymers, which are commonly used as adhesives in packaging.[20]

The FTIR spectrum of the chloroform extract (Figure 2d) also revealed significant peaks of esters. This suggests that the deposited sticks contained a variety of polyester substances with different properties, which cannot be fully extracted by ethanol extraction alone. The absorption peak at approximately 700 $cm^{-1}$ in the FTIR spectrum suggests the existence of aromatic polymers. Additionally, the broadening vibration peak of −OH at 3440 $cm^{-1}$ might signify the presence of carboxyl groups in unsaturated fatty acid esters. The Py-GC-MS analysis (Figure 2f) of the chloroform extract identified styrene, toluene, acrylates, and some olefinic substances (Table 1), suggesting the presence of styrene copolymers and acrylates in the chloroform extract.[19]

Based on the above analysis, it is evident that the predominant sticks entering the papermaking system consist of acrylates. However, variations in the monomers result in differences in the chemical properties of these adhesives. Butyl acrylate (as well as methyl ester, ethyl ester, and 2-ethylhexyl ester) belongs to the soft monomers. It can be copolymerized, cross-linked, and grafted with a variety of hard monomers to synthesize acrylates.[21] Hard monomers include methyl methacrylate, styrene, acrylonitrile, and ethylene vinyl acetate. The wide variety of adhesive formulations presents a significant challenge in managing stickies issues.

**Table 1. Py-GC-MS Analysis of Solvent Extracted Stickies**

| | | compounds | retention time (min) | peak area (%) |
|---|---|---|---|---|
| ethanol extract | 1 | 3-hethyleneheptane | 4.411 | 17.98 |
| | 2 | hexamethylcyclotrisiloxane | 5.081 | 8.01 |
| | 3 | butyl acrylate | 7.040 | 22.65 |
| | 4 | butyl methacrylate | 9.432 | 5.26 |
| | 5 | 2-ethylhexan-1-ol | 11.034 | 15.55 |
| | 6 | 2-ethylhexyl acrylate | 16.863 | 8.17 |
| | 7 | 4-(butoxycarbonyl)-7-methyloctanoate | 27.784 | 22.37 |
| chloroform extract | 1 | toluene | 4.066 | 7.66 |
| | 2 | hexamethylcyclotrisiloxane | 5.105 | 4.49 |
| | 3 | M-xylene | 6.304 | 3.91 |
| | 4 | styrene | 7.058 | 33.77 |
| | 5 | cyclohexanol acetate | 8.791 | 10.71 |
| | 6 | prop-1-en-2-ylbenzene | 9.533 | 7.38 |
| | 7 | D-limonene | 11.052 | 26.68 |
| | 8 | 6-methylheptyl-2-propenoate | 16.869 | 1.97 |
| | 9 | butyl 3-methylpentylglutarate | 27.742 | 3.44 |

**3.2. Mechanism and Application of the "Adhesives Collect Stickies" Strategy.** As shown in Figure 3a, layered structures can be observed on the surface of 2# deposited stickies. This indicates that sticky substances more readily adhere to previously deposited stickies. The 36# deposited stickies were mainly composed of adhesive components. Figure 3b shows that the adhesive components were bonded together without any apparent interfaces due to the molecular compatibility and interdiffusion among adhesive components. This observation inspired development of "adhesives collect stickies".

Figure 4a demonstrates a straightforward method for implementing this strategy, which involves removing microstickies through physical collection by chemically similar adhesives. In this work, GMA, an adhesive component homologous to deposited stickies from the paper mill, was grafted on the surface of PP mat via UV irradiation(Figure 4b).[22] The PP-GMA mat was used as the collector for whitewater from recycled paper pulp.

The key to removing microstickies by adhesion is that the surface of the collector must form a stable bond with them.[23] Most microstickies in whitewater are hydrophobic polymers, so they were attracted to the hydrophobic PP-GMA via van der Waals forces, bonded interdiffusion, and mechanical interlocking (see Figure 4c).[24,25]

The adhesion of stickies to a material promotes the deposition of even more stickies. In summary, microstickies in papermaking whitewater can form stable bonds with surfaces modified with a homologous adhesive and remove them from the system.

**3.3. Physical and Chemical Properties of PP-GMA Mat.** PP nonwoven fabric is made from PP fibers through the needle-punching technique. It has several advantages such as good breathability, low cost, and strong mechanical properties. PP mat can be modified by UV irradiation.[26−29] In this work, the grafting rate of PP-GMA mat was controlled by the



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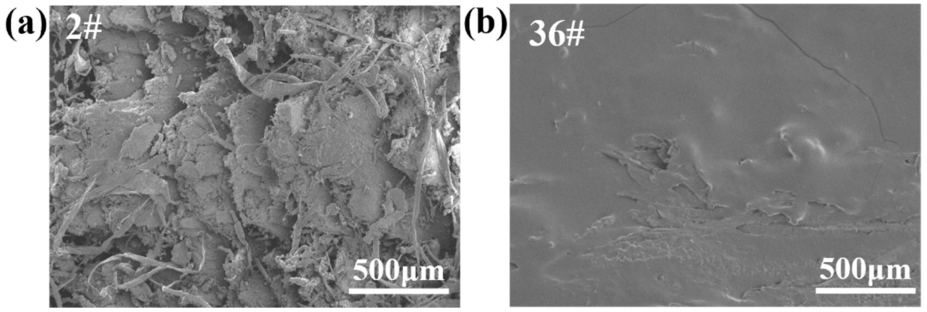


**Figure 3.** (a) SEM images of 2# and (b) 36# deposited stickies.

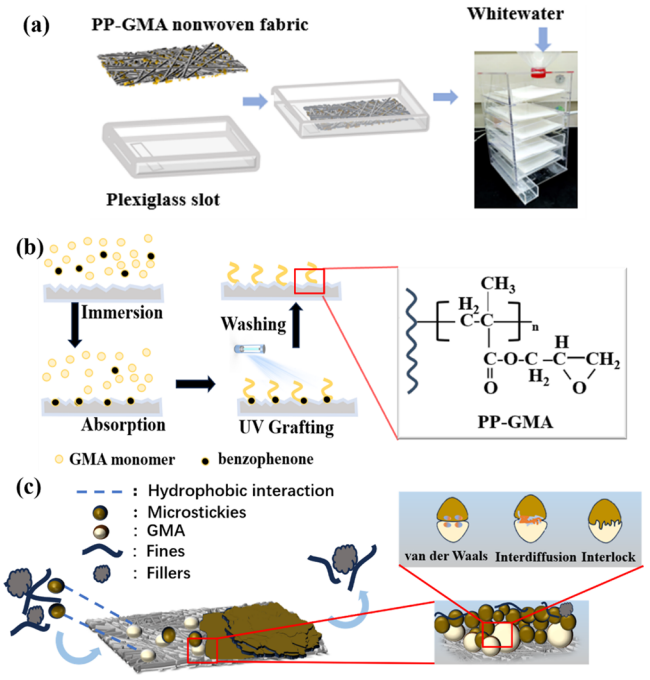


**Figure 4.** Mechanism and application of the "adhesives collect stickies" strategy: (a) Schematic of adhesion experiment. (b) Fabrication of PP-GMA mat. (c) Mechanism of adhesion to remove microstickies.

duration of UV irradiation.[30] The results showed that the PP-GMA mat with a 10% grafting rate of GMA was obtained by UV irradiation for 10 min.

Figure 5a shows the FTIR spectrum of the PP mat before and after modification and washing. The grafting of GMA was proven by the appearances of the carbonyl peak (C═O) at 1732 $cm^{-1}$ and the C−O vibration peaks at 1257 and 1170 $cm^{-1}$ in the PP-GMA sample. The water contact angle of the PP mat was 92.9° (Figure 5a), showing a certain degree of hydrophobicity. The GMA grafting resulted in an increase in hydrophobicity of the polypropylene fibers, raising the water contact angle to 113.5° (Figure 5a). Figure 5b,c shows the surface morphology images of the original PP and PP-GMA mats. The PP fibers exhibited smooth surfaces. After GMA grafting, the PP-GMA fibers showed a rough surface texture. Increased fiber surface roughness provides more favorable conditions for the adhesion of microstickies.

**3.4. Collection Experiments.** Acrylate adhesive (commonly used in paper packaging), rosin resin (typically found in wood), and styrene−butadiene latex (SBR, a commonly used papermaking chemical additive) were selected as model stickies.[31] As shown in Figure 6a, the rosin resins and acrylic adhesive exhibit the FTIR spectrum typical of esters, with the absorption bands at 1735 $cm^{-1}$ due to the C═O stretching and at 1260 and 1025 $cm^{-1}$ due to the C−O stretching of the ester groups. The broadened vibration peak of −OH at 3300 $cm^{-1}$ may signify the presence of carboxyl groups in unsaturated fatty acid esters. The FTIR spectrum of SBR was dominated by characteristic peaks of aromatic hydrocarbons, which differed significantly from the spectrum of the other samples. GMA is a fundamental ingredient utilized in manufacturing acrylate adhesives,[22] so the PP-GMA mat showed similar FTIR characteristic peaks to those of acrylate adhesive (Figure 6a).

The effectiveness and selectivity of our strategy were tested by using PP-GMA mats to collect model stickies from the suspension. As shown in Figure 6b, the PP-GMA mat displayed the best adhesion efficiency for the acrylate adhesive. After exposure to the fiber mat, the total volume of the acrylate adhesive in the suspension decreased by 58.3%, while the total

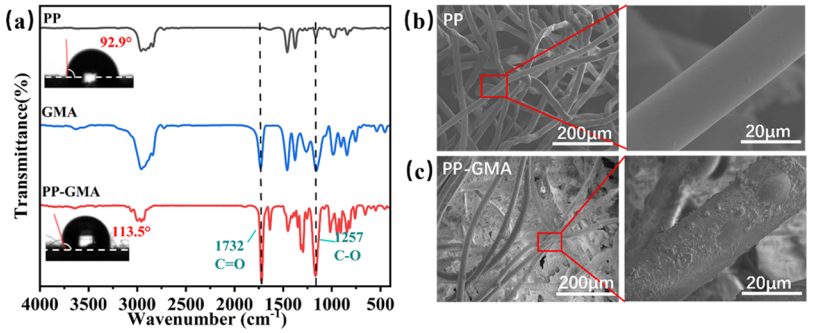


**Figure 5.** Characterization of PP mat before and after modification: (a) FTIR spectrum of PP mat, GMA, and PP-GMA mat; water contact angle of PP mat and PP-GMA mat. (b) SEM images of PP mat. (c) SEM images of PP-GMA mat.



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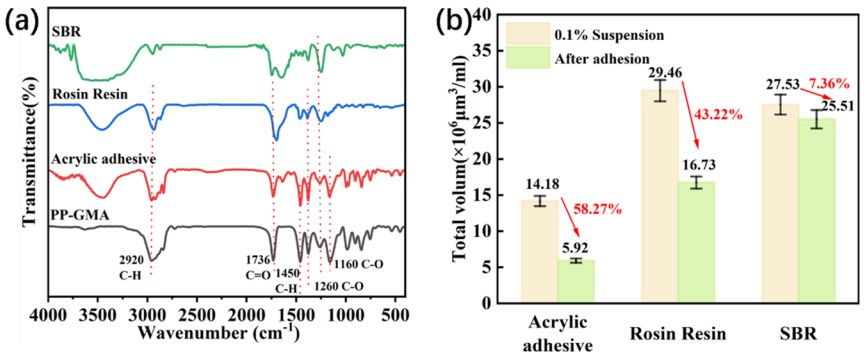


**Figure 6.** Analysis of PP-GMA mat to adhere model stickies: (a) FTIR spectra and (b) volume changes of model stickies after adhesion.

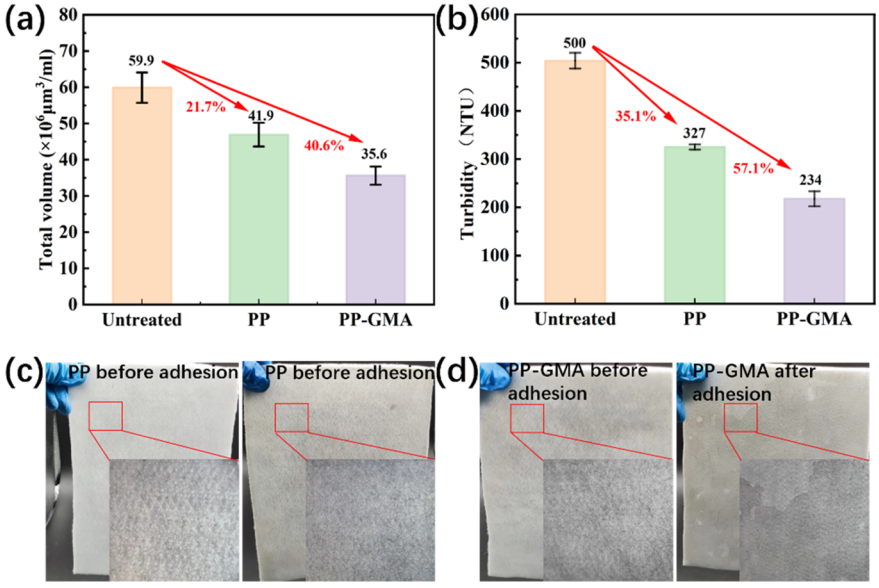


**Figure 7.** Adhesion experiment of whitewater: (a) Volume changes of microstickies in whitewater. (b) Turbidity changes of whitewater. (c) Pictures of PP mat before and after adhesion. (d) Pictures of PP-GMA mat before and after adhesion.

volume of the rosin resin decreased by 43.2%. In contrast, the adhesion efficiency of SBR was poor, with an adhesion removal efficiency of only 7.4%. These results show that a mat with an acrylate surface is good at collecting chemically similar adhesive particles, but the interaction with a chemically different adhesive is much weaker.

The effectiveness of this strategy for whitewater from paper mills was demonstrated by adhesion experiments with whitewater at a flow rate of 3 L/min. As shown in Figure 7a,b, the volume of microstickies and turbidity of whitewater after exposure to unmodified PP mat were reduced by 21.7% and 35.1%, respectively. When exposed to the PP-GMA mat, these decreased by 40.6% and 57.1%, respectively. Since other substances besides microstickies in whitewater also adhered to collector surfaces, the decrease in turbidity was greater than that of the microstickies volume. The turbidity essentially followed the same trend as the changes in the microstickies volume.

Figure 7c,d depicts images of the mats before and after exposure to whitewater. It can be observed that deposits on PP mats were scattered, while those on the PP-GMA mats were distributed in larger patches, covering nearly the entire surface of the mat. The surface modification provided adhesive sites for collecting microstickies from whitewater, which continues to provide sites for further agglomeration. These results confirm the effectiveness of the "adhesives collect stickies" strategy for controlling microstickies in papermaking whitewater.

The collection experiments were conducted in a continuous fashion to consider the scalability. Within the flow rate range of 3−15 L/min, whitewater can consistently achieve full contact with the collector. As shown in Figure 8a, removal efficiency of particles by PP-GMA mats remained stable and in the range of 40.6−49.6%. Additionally, Figure 8d illustrates that the turbidity of the whitewater correlates with changes in microstickies volume, with observed turbidity reduction ranging between 34.8% and 44.3%.

The particle size of the microstickies is an important factor affecting their removal from whitewater.[32] As shown in Figure 8b,c, the total particulate number of whitewater decreased and then increased, while the average particle size showed no significant trend. This indicates that as flow rate increased, more microsticky particles were likely to adhere to the adhesion materials, but some aggregated microsticky particles may be dislodged by fluid shear.

Figure 8e,f show that larger microsticky particles (sized between 60 and 100 $\mu$m) were more likely to adhere to the mat when the flow rate was below 6 L/min. The proportion of small microstickies particles (<1 $\mu$m) in the whitewater increased, leading to a significant decrease in total particles



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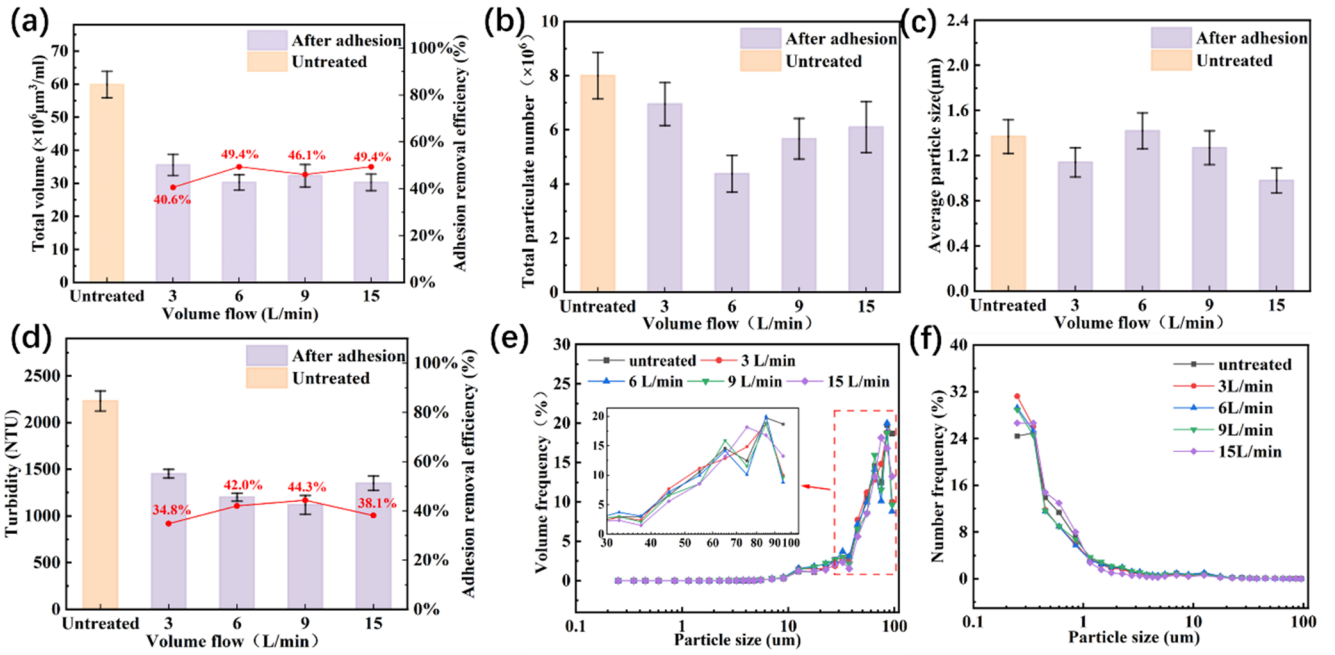


**Figure 8.** Changes of microstickies after adhesion experiments in 1 L whitewater samples at different flow rates: (a) total volume of microstickies, (b) total particulate number of microstickies, (c) average particle size of microstickies, (d) turbidity of whitewater, (e) frequency distribution of the volume of microstickies, and (f) frequency distribution of the number of microstickies.

and an increase in average particle size. Furthermore, with increasing flow rate, the proportion of larger microstickies particles increased while the average particle size decreased. This suggests that smaller microstickies particles aggregated into larger ones.

In this work, adhesion occurred as whitewater flowed over the surface of the mat. Excessive flow rate can lead to inadequate contact between the whitewater and the mat. Furthermore, a high flow rate increases the likelihood of microsticky particles accumulating on the collector being dislodged by strong fluid shear forces. Therefore, it is imperative to identify an appropriate flow rate range to ensure that whitewater microstickies adhere and remain adhered to the material's surface. For the experimental device in this work, the optimal collection efficiency was achieved at a flow rate of 6 L/min, but exhibited a good efficiency over the flow rate range of 3−15 L/min.

To enhance the overall removal efficiency of microstickies, employing multiple devices in series is a viable option. Given the complex nature of the adhesive composition, a single collector may not suffice. In such scenarios, utilizing a range of surface modifications may allow the removal of more kinds of microstickies. In summary, the "adhesive collect stickies" strategy offers a potential approach for removing microstickies from whitewater loops, reducing the impact of stickies in the paper industry.

## 4. CONCLUSIONS

In this study, we have proposed a strategy for collecting whitewater microstickies by grafting homologous adhesive components onto surfaces of PP-GMA mats. These mats achieved an adhesion efficiency of 58.3% for acrylic adhesive from suspension samples. These mats were also shown to efficiently remove microstickies (40.6%) from paper mill samples containing acrylates. We demonstrated a continuous flow cell with stable collection efficiency (40.6−49.4%) for flow rates of 3 to 15 L/min. Coupling devices with surface modifications tuned to different adhesive materials may allow development of a process that is effective at removing a wider range of microstickies. "Adhesive collects stickies" is one of the only methods for removing microstickies from mill whitewater loops without disrupting the chemical environment of the papermaking system.

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### Author Contributions

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Chen, P.; Sauerwein, M.; Steuer, B. Exploring Greenhouse Gas Emissions Pathways and Stakeholder Perspectives: In Search of Circular Economy Policy Innovation for Waste Paper Management and Carbon Neutrality in Hong Kong. *J. Environ. Manage.* **2023**, *341*, No. 118072.
(2) Monte, M. C.; Sanchez, M.; Blanco, A.; Negro, C.; Tijero, J. Improving Deposition Tester to Study Adherent Deposits in Papermaking. *Chem. Eng. Res. Des.* **2012**, *90*, 1491−1499.
(3) Zhang, Z.; Lan, D.; Zhou, P.; Li, J.; Yang, B.; Wang, Y. Control of Sticky Deposits in Wastepaper Recycling with Thermophilic Esterase. *Cellulose* **2017**, *24*, 311−321.
(4) Hubbe, M. A.; Rojas, O. J.; Venditti, R. A. Control of Tacky Deposits on Paper Machines - A Review. *Nord. Pulp Pap. Res. J.* **2006**, *21*, 154−171.
(5) Liu, Z.; Li, G.; Zhang, F.; Wu, J. Enhanced Biodegradation Activity Towards Poly(Ethyl Acrylate) and Poly (Vinyl Acetate) by Anchor Peptide Assistant Targeting. *J. Biotechnol.* **2022**, *349*, 47−52.
(6) Kim, C.; Lee, M.; Lee, J.; Ryu, J.; Park, J.; Park, J. Comparison of the Effect of Tmp Pitch Control Agents with Different Mechanisms. *Wood Fiber Sci.* **2022**, *54*, 111−121.
(7) Gao, Y.; Qin, M.; Yu, H.; Zhang, F. Effect of Heat-Dispersing on Stickies and their Removal in Post-Flotation. *Bioresources* **2011**, *7*, 1324−1336.
(8) Gribble, C. M.; Matthews, G. P.; Gantenbein, D.; Turner, A.; Schoelkopf, J.; Gane, P. A. C. Adsorption of Surfactant-Rich Stickies onto Mineral Surfaces. *J. Colloid Interface Sci.* **2010**, *352*, 483−490.
(9) Genest, S.; Petzold, G.; Schwarz, S. Removal of Micro-Stickies from Model Wastewaters of the Paper Industry by Amphiphilic Starch Derivatives. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *484*, 231−241.
(10) Gribble, C. M.; Matthews, G. P.; Gantenbein, D.; Turner, A.; Schoelkopf, J.; Gane, P. A. C. Adsorption of Surfactant-Rich Stickies onto Mineral Surfaces. *J. Colloid Interface Sci.* **2010**, *352*, 483−490.
(11) Xu, Y. T.; Cao, X. L.; Houtman, C.; Li, B.; Mo, W. X.; Li, X. H. Effects of Metal Surface Morphology on Deposition Behavior of Microstickies from Papermaking White Water. *Tappi J.* **2023**, *22*, 466−473.
(12) Doshi, M.; Dyer, J.; Aziz, S.; Jackson, K.; Abubakr, S. Quantification of Micro Stickies. *Prog. Pap. Recycl.* **1997**, *7*, 79−82.
(13) Dhyani, A.; Wang, J.; Halvey, A. K.; Macdonald, B.; Mehta, G.; Tuteja, A. Design and Applications of Surfaces that Control the Accretion of Matter. *Science* **2021**, *373*, No. eaba5010.
(14) Kavaklı, C.; Barsbay, M.; Tilki, S.; Güven, O.; Kavaklı, P. A. Activation of Polyethylene/Polypropylene Nonwoven Fabric by Radiation-Induced Grafting for the Removal of Cr(Vi) From Aqueous Solutions. *Water, Air, Soil Pollut.* **2016**, *227*, 473.
(15) Guliakova, A. A.; Galikhanov, M. F.; Galeeva, L. R.; Gilfanova, S. V.; Fang, P. Investigation of Electret and Filtering Properties of Polypropylene-Based Nonwoven Fabrics and its Composites with 2 vol% of Silicon Dioxide Inclusions. *Ieee T. Dielect. El. In.* **2020**, *27*, 1656−1661.
(16) Zheng, Y.; Gurgel, P. V.; Carbonell, R. G. Effects of UV Exposure and Initiator Concentration on the Spatial Variation of Poly(Glycidyl Methacrylate) Grafts on Nonwoven Fabrics. *Ind. Eng. Chem. Res.* **2011**, *50*, 6115−6123.
(17) Wang, Z. W.; Li, B.; Wu, S. B.; Lu, P. Physicochemical Properties Analysis and Size Distribution Research of Microstickies in Whitewater. *Bioresources* **2012**, *7*, 5794−5808.
(18) Tang, Y. N.; Li, B.; Geng, S. F.; Houtman, C.; Wu, S. B. Size Distribution Analysis of Microstickies Treated by Enzyme Mixtures in Papermaking Whitewater. *Tappi J.* **2019**, *18*, 183−192.
(19) Miranda, R.; Balea, A.; Blanca, E. S. D. L.; Carrillo, I.; Blanco, A. Identification of Recalcitrant Stickies and their Sources in Newsprint Production. *Ind. Eng. Chem. Res.* **2008**, *47*, 6239−6250.
(20) Wang, Y.; Marcello, C.; Sawant, N.; Salam, A.; Abubakr, S.; Qi, D.; Li, K. Identification and Characterization of Sticky Contaminants in Multiple Recycled Paper Grades. *Cellulose* **2023**, *30*, 1957−1970.
(21) Jerome, R.; Teyssie, P.; Vuillemin, B.; Zundel, T.; Zune, C. Recent Achievements in Anionic Polymerization of (Meth)Acrylates. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 1−10.
(22) Jiang, L.; Liu, Z. M.; Hu, K.; Kong, W. B.; Lei, J. X. Preparation and Properties of Environment-Friendly Acrylic Latex Laminating Adhesives Applied in Plastic/Plastic Composite Films. *J. Adhes. Sci. Technol.* **2019**, *33*, 2−17.
(23) Baldan, A. Adhesively-Bonded Joints and Repairs in Metallic Alloys, Polymers and Composite Materials: Adhesives, Adhesion Theories and Surface Pretreatment. *J. Mater. Sci.* **2004**, *39*, 1−49.
(24) Baldan, A. Adhesion Phenomena in Bonded Joints. *Int. J. Adhes. Adhes.* **2012**, *38*, 95−116.
(25) Thenmozhi, R.; Thilagavathi, G. Investigations on Kapok/Polypropylene Needle Punched Nonwoven for Thermal Resistance Applications. *J. Nat. Fibers* **2023**, *20*, No. 2146247.
(26) Yang, J. M.; Lin, H. T.; Wu, T. H.; Chen, C. C. Wettability and Antibacterial Assessment of Chitosan Containing Radiation-Induced Graft Nonwoven Fabric of Polypropylene-*G*-Acrylic Acid. *J. Appl. Polym. Sci.* **2003**, *90*, 1331−1336.
(27) Castell, P.; Wouters, M.; de With, G.; Fischer, H.; Huijs, F. Surface Modification of Poly(Propylene) by Photoinitiators: Improvement of Adhesion and Wettability. *J. Appl. Polym. Sci.* **2004**, *92*, 2341−2350.
(28) Pan, K.; Gu, H.; Cao, B. Interfacially Polymerized Thin-Film Composite Membrane on UV-Induced Surface Hydrophilic-Modified Polypropylene Support for Nanofiltration. *Polym. Bull.* **2014**, *71*, 415−431.
(29) Amintowlieh, Y.; Tzoganakis, C.; Penlidis, A. The Effect of Depth and Duration of UV Radiation on Polypropylene Modification Via Photoinitiation. *J. Appl. Polym. Sci.* **2014**, *131*, 41021.
(30) Zheng, Y.; Liu, H.; Gurgel, P. V.; Carbonell, R. G. Polypropylene Nonwoven Fabrics with Conformal Grafting of Poly(Glycidyl Methacrylate) for Bioseparations. *J. Membr. Sci.* **2010**, *364*, 362−371.
(31) Benecke, F.; Gantenbein, D.; Schoelkopf, J.; Gane, P.; Gliese, T. Organic Contaminants in Recycled Paper: A Model Study of the Adsorbent Properties of Talc for Idealised Component Suspensions. *Nord. Pulp Pap. Res. J.* **2009**, *24*, 219−224.
(32) Li, B.; Wang, Z.; Wu, S.; Liu, J.; Cheng, J. Effects of Adhesive Aging on the Characteristics of Stickies and their Removal During Paper Recycling. *Ind. Eng. Chem. Res.* **2013**, *52*, 9698−9704.


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