Identification and Characterization of Sticky Contaminants in Multiple Recycled Paper Grades

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Research Article

Keywords: Sticky contaminants, Paper recycling, FT-IR, GC-MS, SEM, Solvent extraction

Posted Date: June 14th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1727996/v1

Abstract

Organic sticky contaminants represent one of the biggest technical challenges in the paper recycling process. These contaminants reduce paper strength, cause plugging of wires and felts, and stick to or deposit on machine parts affecting the runnability of the paper machine. The removal of these sticky contaminants is difficult to achieve along the process due to the heterogeneous nature of these organic contaminants. In this study, the nature of sticky contaminants in multiple wastepaper grades was analyzed and characterized using screening, solvent extraction with subsequent analysis such as FT-IR, GC-MS, and SEM.

The content of stickies in wastepaper varies among different paper grades and their recovery methods. The majority of wastepaper grades collected from a recycled paper mill contains 3–5 wt% stickies, while a sample from a curb side collection from a residential area contains about 15 wt% stickies. Polyvinyl acetate (PVA) polymers, styrene butadiene rubber (SBR), paraffin waxes and polyamines are the major components in the extracted sticky contaminants. In addition, these stickies deposit heavily on fibers surface leading to high negative charge in fibers suspension ranging between 2 ~ 4.5 μeq/L. It is expected that these findings will assist addressing the knowledge gaps in understanding the nature of stickies and their behaviors, and to eventually develop highly efficient technologies for contamination removal in the paper recycling process.

Introduction

Recovered paper plays an increasingly important role in global paper industry as paper recovery rates continue to increase each year in most parts of the world. As a great substitute for virgin fibers, it provides savings on energy consumption and reductions on GHG emissions during papermaking process. However, the use of recovered paper is limited by its low quality due to the presence of a variety of contaminants, which can be classified according to their sources, i.e. organic, inorganic and microbiological contaminants (Hubbe et al., 2006). Although cleaning techniques are implemented in the papermaking process, some contaminants can carry through or even build up during the manufacturing process. The term “stickies” is commonly used to describe these tacky substances.

Stickies represent one of the biggest problems in paper recycling process. These contaminants inhibit inter-fiber bonding which directly impacts the physical strength of the recovered paper products (Douek et al., 2003). In addition, the presence of stickies in the paper machine also causes plugging of wires and felts, leading to reduction on the water drainage of the fiber suspension. Furthermore, the contaminants stick to process equipment, such as the press rolls and the dryers, causing mechanical problems of runnability (Fogarty, 1993; Maher et al., 2007). Ultimately, all these problems lead to low quality products and higher cost for the paper manufacturers. Therefore, the efficient removal of these sticky contaminants has become increasingly critical to paper industry. To improve the removal of sticky contaminants and eventually extend the utilization of recovered paper, the nature of these stickies and their characterizations need to be investigated.

The sticky contaminants are commonly classified based on particle sizes as “macrostickies” and “microstickies” (Doshi, Blanco, et al., 2003). This classification defines “macrostickies” as solid contaminants that are retained on mesh and have a diameter of about 100–150 um. This kind of contaminants is generally monitored to determine the contamination removal efficiency of the process units. On the other hand, the contaminants with a diameter of less than 100 um are defined as “microstickies”. Microstickies can be further classified into suspended and dispersed (5–100 um), and colloidal and dissolved stickies (< 5 um). However, this classification by size is not enough. From a chemical point of view, stickies consist of a very broad range of components including high and low molecular weight organic compounds, and natural and synthetic polymers. They are typically derived from a combination of contaminant sources, e.g. adhesives, coating materials, ink residues, processing chemicals and wood derivatives (X. Y. Guo, 1996). Adhesives are generally considered to be the most detrimental source for the formation of deposits during papermaking process (Blanco et al., 2002; Hamann & Strauss, 2003). The predominant polymers used for adhesives include polyvinyl acetate (PVA), polyacrylates, styrene butadiene rubber (SBR), ethylene vinyl acetate (EVA), polyamide, polyvinyl alcohol, styrene butadiene styrene (SBS), synthetic resins, etc (Doshi & Dyer, 2007; Gribble et al., 2010). Coating binders are a secondary source for the generation of stickies. One of the most predominant compounds is SBR latex; while PVA and polyvinyl acrylate are also commonly used (Laudone et al., 2004; Vahasalo & Holmbom, 2006). As tacky contaminants from printing inks, toners using SBR and polyvinyl acrylate contain the same chemical components as adhesives. Wood extractive, rosins and wet strength additives are other possible causes of stickies deposits.

The heterogeneous nature of sticky contaminants makes their identification and characterization very difficult using simple methods (Blazey et al., 2005; Holbery, 2000). The determination typically requires complex multi-step procedures starting with fractionation of stickies, and solvent extraction for quantification, followed by characterization using several analytical techniques (Doshi, Moore, et al., 2003; X. Y. Guo, 1996; Holbery, 2000; Leclerc, 2000). Gravimetric extraction with an organic solvent is commonly used to isolate hydrophobic substances from the fibers. It is the basis of stickies measurement method, the result is, however, very dependent on the solvent used. Most commonly used solvents include dichloromethane (DCM), dimethyl formamide (DMF), trichloroethane (TCE), acetone, and tetrahydrofuran (THF) (Cao & Heise, 2005; Dionne et al., 2006; Hamann, 2005; Holmbom, 1997; Lenes et al., 2001; Sjoestroem et al., 1987). Among them, THF and DCM has demonstrated to be more selective to stickies which obtain higher yields, but DCM was reported also dissolve the non-sticky components such as the lignin components, e.g., dimethylformamide (MacNeil et al., 2004, 2006). Therefore, THF was selected in this study. Subsequently, multiple analytical techniques have been applied for the characterization of stickies including Fourier-transform Infrared Spectroscopy (FTIR), Gas Chromatography/Mass Spectrometry (GC/MS), Gel Permeation Chromatography (GPC), Thermogravimetry (TGA), Differential Scanning Calorimetric Analysis (DSC) and Scanning Nuclear Resonance (NMR) (Biermann & Lee, 1990; Gao et al., 2012; Holbery, 2000; Sjostrom & Holmbom, 1988; Zheng et al., 2002). Fourier Transform Infra-Red spectroscopy (FT-IR) is commonly used in identification of sticky substances in many studies (Allen & Ouellet, 2006; Cao & Heise, 2005; Delagoutte et al., 2003).

Johansson et al. were able to quantify stickies with IR analysis and multivariate data analysis of the spectra (Johansson et al., 2003). Gas Chromatography (GC) combined with Mass Spectrometry (MS) can detect and quantify organic components, and it has been used for quantifying wood extractives (Guo & Douek, 1995; Orsa, 1994). For investigating stickies, a pyrolysis unit is needed on GC/MS. In pyrolysis, stickies are decomposed into individual compounds and are then identified and quantified. Py-GC/MS has been used by many authors (Holmbom, 1997; Lenes et al., 2001; Odermatt et al., 2005, 2007; Öqvist et al., 2005; Sjoestroem et al., 1987). In addition, Sjöström et al. used HPLC for separating stickies from other substances with a Size Exclusion Column (SEC), where substances are separated based on molecular size (Sjoestroem et al., 1987). They used IR and Py-GC/MS for the polymeric fraction and GC for the low molecular size fractions. Holmbom also separated polymers from other hydrophobic substances with HPLC-SEC and quantified these polymers with Py-GC/MS (Holmbom, 1997).

Although multiple methods have been proposed for the characterization of stickies, the establishment of a universal method is not completed, making it difficult to study the evolution of stickies content along the process and the removal efficiency of the different stages (Blanco Suárez et al., 2007; Doshi, Blanco, et al., 2003; Doshi, Moore, et al., 2003). Additionally, these methods mainly focus on the analysis of macrostickies, but no generally accepted standard method for the determination of microstickies is available. Furthermore, being the main origin of potential deposits in paper recycling process, microstickies constitute 70–90% of the total stickies while remaining recalcitrant in the paper recycling process and not being removed effectively (Delagoutte et al., 2003; Delagoutte & Brun, 2005; Johansson et al., 2003; Sarja et al., 2006). In this sense, the identification and characterization of the most problematic contaminants is the key for reducing contamination (Licursi et al., 2016; Miranda Carreño et al., 2008). Therefore, in this research, an integrated chemical approach by solvent extraction and subsequent characterization of the extracted stickies is proposed which allows the analysis of stickies at all dimensions. In this case, multiple analytical techniques are applied for the characterization of stickies, including FT-IR, GC-MS, colloidal titration, etc. Through full characterization of sticky contaminants in multiple recycled paper grades, it is expected that the findings of this research will provide information to address the knowledge gaps in understanding the nature of stickies and their behaviors, and to eventually develop highly efficient technologies for contamination removal.

Materials And Methods

Materials

Multiple grades of recycled paper feedstock are obtained from local paper recycling mills and from residential curb-side collection. These include residential wastepaper (Residential), old corrugated containerboard (OCC), recycled boxboard cuttings (Box), recycled kraft linerboard (Kraft Liner), printed bleached kraft paper (Bleached Kraft), used office paper (Mixed Office), and old newsprint paper (ONP). Residential mainly consists of food containers such as burger boxes, pizza boxes, food wrapping papers, and etc. These papers are highly contaminated with oil and grease. OCC includes mostly post-consumer packaging materials, such as containerboards obtain from wholesale stores. Box consists cuttings of multiply paperboards that are used in the production of folding paper cartons such as cereal boxes. Kraft Liner is sorted paperboards with Kraft liners, which are mainly from postal packaging boxes. Bleached Kraft are heavily printed sheet with a high calliper, made of bleached sulfite pulp. They are typically used as feedstock for converting mills to make high-grade packaging boxes. Mixed Office is common printing and writing paper, which can be found in typical workplace. ONP is a mixture of used newspaper and old grocery store flyers. Photos of these wastepaper are shown in Fig. 1.

The recycled papers were used as received, and the “as received” moisture content of all grades was determined following TAPPI standard method T412. All chemicals used in this study such as tetrahydrofuran (THF) and poly-DADMAC were purchased from Fisher-Scientific.

Physical characterization of sticky contaminants

Dried recycled fibers were grinded to pass a 0.4mm (40 mesh) screen following TAPPI T257. Ground fibers were utilized to perform solvent extraction of sticky contaminants using conventional laboratory Soxhlet extractor following TAPPI T204. Deionized water (DI water) and tetrahydrofuran (THF) were used as extraction solvents. The fibers were extracted with DI water first and then with THF. Extraction process was maintained for 4 hours (predetermined), and the heat was controlled to provide a boiling rate which cycles the solvent at least 6 times per hour. Solvent was partially evaporated to 20ml in the extraction flask using rotary evaporator, and then transferred to a weighing dish with a small amount fresh solvent. The weighing dish and content were dried in an oven for 1 hour at 105^{o}C ± 3^{o}C, cooled in a desiccator, and weighed to the nearest 0.1mg.

The content of sticky contaminants was calculated using Eq. (1):

$$Contentofstickycontaminants(wt\%) = \frac{W_f - W_e}{W_f} \times 100\%$$

1

where

W_f= oven-dry weight of recycled fibers prior to extraction, g

W_e= oven-dry weight of recycled fibers post extraction, g

The size and number of sticky contaminants in recycled paper were determined by a modified “pick-up” method following TAPPI T277. Handsheets which were made from wastepaper samples were placed between two coated (red) papers. The three sheets were heated and pressed under controlled conditions (7 tons, 177^{o}C) for 5min. Once the coated papers were removed from the handsheet, the coating were picked up by the stickies and a contrast was created on the handsheet, which readily allowed the measurement of area and number of heat-set stickies.

The specific stickies area, specific stickies number, and average stickies size were calculated using the following equations (2), (3), and (4), respectively:

$$S_a = \frac{A}{M}$$

2

$$S_n = \frac{N}{M}$$

3

$$D = \frac{S_a}{S_n}$$

4

where

Sa = Specific stickies area, mm^2/kg

Sn = Specific stickies number, kg^{-1}

D = Average stickies size, mm^2

A = Total area of stickies, mm^2

M = Total O.D. mass of handsheet, kg

N = Total stickies count.

FT-IR analysis

The FT-IR spectra of sticky contaminants were identified using a Perkin Elmer Spectrum 100 instrument with attenuated total reflection accessory. The sticky samples were placed in close contact with the internal reflection element to perform the characterization. The acquisition of each spectrum has provided 12 scans in the range 800–4000 cm^{-1}, with a resolution of 4 cm^{-1}. FT-IR spectra were compared with those of the electronic library of the instrument and with ones reported in the literatures.

GC-MS analysis

Extracted stickies samples were analyzed using an Agilent 6890 gas chromatograph coupled to an Agilent 5973 Mass Spectrometer. Analyte separations were accomplished in an Agilent J&W HP-5MS UI column (5% phenyl methyl siloxane, 30M x 0.25 mm x .25 um) using the following temperature program: 50^{o}C, hold 3min, 10^{o}C per minute to 310^{o}C, and hold for 9 minutes. The split less injector was held at

300°C, carrier gas was helium at a constant flow rate of 1 ml/min. The MSD transfer line temperature was held at a constant 310°C, the MSD ion source at 230°C and the MSD quadrupole at 150°C. After a 3-minute solvent delay, full scan mass spectra were collected from 35 to 750 m/z. Peak identification was accomplished by comparison with a NIST (National Institute of Standards and Technology) 2008 library.

SEM

The recycled fibers and sticky contaminants were observed by Field Emission Scanning Electron Microscopy (FE-SEM) (Jeol JSM-IT200, Japan). Dried wastepaper samples were immobilized on conductive tape and coated with thin gold layer. The images were observed at an accelerating voltage of 10 kV with the resolution of 0.1 nm.

Colloidal titration

The water-soluble sticky contaminants typically possess negative charges. These dissolved colloidal substances (DCS) also known as anionic trash, were quantified through colloidal titration The capability of DSC to absorb polyelectrolyte of opposite charge, which in this case, is the amount of cationic polymer required to neutralize the sample, was determined using a Mütek PCD-03 charge detector. The streaming current method was followed to determine the endpoint of colloidal titration.

Recycled papers were disintegrated into 0.1% fiber suspension and denoted as total stock (total charge). Clear liquid samples, taken from the centrifuged total stock, were denoted as dissolved substances (dissolved charge). The volume of poly-DADMAC (cationic titrant) consumed to achieve zero potential was recorded. The specific charge quantity (μeq/L) was calculated using Eq. (5):

$$q = \frac{(V - V_b) \times C}{wt}$$

5

where

q = specific charge quantity of sample, μeq/L

V = consumed titrant volume, ml

V_b = consumed titrant volume in blank test, ml

C = specific charge quantity of titrant, μeq/L

wt = volume of tested liquid sample, ml

Results And Discussion

Observation of sticky contaminants

Pictures of the recycled paper raw materials collected from local paper mills are shown in Fig. 1, and pictures of the visible contaminants are shown in Fig. 2. It is noted that these recycled papers contain multiple sources of sticky contaminants, including but not limited to food residue (oil/grease), tape and label residue (adhesives), hot melt adhesives, and printed ink (chemical substances). These contaminants vary in size, shape, and chemical compositions, and thus are difficult to remove through mechanical process.

Field Emission Scanning Electron Microscopy (FE-SEM) was utilized to further observe the sticky contaminants attached on paper surface. Recycled OCC materials were analyzed to observe adhesives attached on fiber surface. The SEM images are shown in Fig. 3. In Fig. 3(a), on the surface of a clean recycled OCC paper, the fibers are clearly visible without any major contaminant. The fiber wall structure and some microfibrils can be clearly observed even with paper coating pigments and fillers attached to fiber surface. In the contrary, at lower magnification in Fig. 3(b), recycled fibers are completely covered by a layer of plastic-like substance which is the adhesive polymer. At high magnification in Fig. 3(c), fiber wall structure, microfibrils, and coating particles are completed blocked by contaminants.

SEM images of contaminants on Residential wastepaper are shown in Fig. 4. The primary contaminants on residential wastepaper are food residue, e.g., oil and grease. Unlike adhesive contaminants on recycled OCC, these oil contaminants attach to fibers surface in the form of small particles or wrap fiber wall structure in the form of thin films. The presence of these contaminants significantly reduces inter-fiber contacting areas, occupies hydroxyl groups and thus leads to reductions in recycled paper strength.

Size, number, and quantity of sticky contaminants in recycled papers

Sticky contaminants in multiple recycled paper grades were extracted using water and THF following TAPPI T204, and the weight percentage of stickies in fibers were calculated using Eq. (1). The results of all recycled paper grades are indicated in Table 1.

Among all seven wastepaper grades, the content of sticky contaminants in Residential reaches up to 14.8%, which is the highest among all grades. This is mainly contributed by the noticeable amount of grease and oil from food residues on residential wastepapers. Approximately 50% of the food residue contaminants dissolves in water, and the rest can be extracted using THF. OCC material contains 4.5% stickies in total, with a majority only soluble in organic solvent THF. It is observed from the appearance, OCC stock is contaminated with significant numbers of labels and packaging tapes, both involving the use of pressure sensitive adhesives. These organic polymers have low solubility in water. This explains the relatively high level of THF soluble stickies, 3.6%. Kraft liners, Bleached kraft, ONP and Mixed office contain 5.1%, 5.3%, 3.5%, and 3.6% stickies in total, respectively. The majority of these stickies are soluble in water. They are likely contributed by ink substances, or other papermaking additives. ONP and Mixed office paper have the lowest stickies content among all recycled grades besides of Box. From the appearance, both of them are much cleaner source of fibers with only lightly printed with ink. Box paper barely contains any solvent extractable sticky contaminants.

Table 1
Quantity of sticky contaminants in recycled papers.

Recycled paper grades	Stickies content (wt%)			In reference papers
	Water extractives	THF extractives	Total	
Residential	7.7	7.1	14.8	n.a.
OCC	0.9	3.6	4.5	5 ~ 6% *
Kraft Liner	5.1	< 0.1	5.1	
Bleached Kraft	5.3	< 0.1	5.3	n.a.
Box	< 0.1	< 0.1	< 0.1	n.a.
ONP	2.9	0.6	3.5	1.1% **
Mixed Office	3.6	< 0.1	3.6	
*(Licursi et al., 2016)				
**(Blanco Suárez et al., 2007)				

Table 2
Size and number of stickies in wastepaper

	Specific stickies area (mm^2/kg)	Specific stickies number (kg^{-1})	Average stickies size (1/1000 mm^2)
Residential	377	32167	11.7
OCC	127	13833	9.3
Kraft Liner	98	7833	12.4
Bleached Kraft	53	8000	6.6
Box	18	3000	5.9
ONP	22	5000	4.4
Mixed Office	30	4167	7.3

The physical properties of sticky contaminants presented in recycled paper sheets, including size and number, were determined using a thermal pick-up method, and the resulted are presented in Table 2. The specific number of stickies and the specific heat-set area of stickies in paper sheets are in agreement with the content of stickies presented above. As the most contaminated wastepaper, Residential grade contains over 32000 stickies/kg fibers with a total area of 377 mm^2. In addition, these stickies counts are relatively large having an average size of 0.0117 mm^2. OCC grade contains nearly 14000 stickies/kg fibers with a total area of 127 mm^2, while the average size of the stickies is around 0.009 mm^2. Kraft liner grade contains around 7800 stickies/kg fibers, which is much less than that of Residential and OCC grade, however, the average size of these stickies is about 0.0124 mm^2, which is the largest among all wastepaper grades. Bleached kraft grade also contains 8000 stickies/kg fibers with a much smaller size of 0.007 mm^2. The stickies counts in Box, ONP, and Mixed office grades are in the lower range between 3000–5000, with an average size between 0.004-0.007mm^2.

Chemical compositions of sticky contaminants

The chemical compositions of the extracted sticky contaminants from each recycled paper grade were characterized using FT-IR and GC-MS. The FT-IR spectra of stickies extracted from each recycled paper grade are presented in Fig. 5 and Fig. 6.

The FT-IR spectrum of THF extracted stickies from OCC and Residential are shown in Fig. 5, respectively. In the FT-IR profile of stickies extracted from OCC, it is first to observe the strong absorption at about 1735 cm^{-1} due to the C = O stretching of the acetate group; and the bands at about 1260 cm^{-1}, 1160 cm^{-1} and 1025 cm^{-1} due to the C-O stretching of the ester group. Typical C-H stretching absorption bands of alkane are observed at between 2960 cm^{-1}, 2920 cm^{-1} and 2850 cm^{-1}, respectively. C-H bending absorption are observed at 1460 cm^{-1} and 1365 cm^{-1}. These results indicate the presence of polyvinyl acetate (PVA) polymers, which are generally used as adhesives in packaging (Licursi et al., 2016; Miranda Carreño et al., 2008). As also shown in Fig. 5, the extracted stickies from Residential grade presented similar FT-IR profile as that of OCC stickies. Regarding the absorption bands, the presence of esters is observed. Evidence of ester groups is identified by the absorption bands at 1735 cm^{-1} due to the C = O stretching and at 1260 cm^{-1}, 1025 cm^{-1} due to the C-O stretching of the ester groups. These components are likely to be introduced by food residue such as residual cooking oils.

Infrared spectrum of stickies extracted with water from Residential, Mixed Office, ONP, Kraft Liner, and Bleached Kraft grades are presented in Fig. 6, respectively. These profiles indicate the presence of ink components with absorption band at 1560 cm^{-1} which is assigned to the aromatic absorbance of gallate, and absorption band at 1410 cm^{-1} which is contributed by the symmetric stretch of iron (III)-gallate complex. In addition, the absorption band at 1125 cm^{-1} and 1020 cm^{-1} can be assigned to vibrations of C-O bonds of ester group. Furthermore, the broad absorption band at 3275 cm-1 represents O-H stretching in phenol structure, and the absorption band of C-H stretching is observed at 2920 cm^{-1}. The infrared spectrum analysis indicates the major contribution of water extracted stickies of recycled papers are ink residues.

The GC-MS chromatogram of solvent extracted stickies from OCC is presented in Fig. 7, and the major components are presented in Table 3. The components in extracted stickies can be concluded into five groups. First, dimethylamine and dimethyl propylamine are identified in the GC-MS spectrum at 4.0 min and 6.1 min. They are the monomer units of polyamines, which is a commonly used polymer in papermaking process. The quaternary ammonium group in polyamine structure maintains strong cationic charge in most papermaking conditions, and thus are used extensively for neutralizing excess anionic colloidal charge and establishing anchoring points for anionic retention aids. Second, the two peaks at 7.6 min and 7.8 min represent methyl styrene, which is a monomer compound in styrene acrylates. Styrene acrylates are commonly used as a sizing agent in papermaking process to increase resistance to water penetration. In addition, methyl styrene is also used as the monomer unit for the synthesis of styrene butadiene rubber (SBR), which is a major component in hot melt adhesive as a thermoplastic elastomer. Furthermore, peaks at 10.4 min and 15.0 min indicate the presence of cyclosiloxanes, which is a silicone resin material being widely applied as coating ingredients. Moreover, peaks from 24 min to 35 min are paraffin wax compounds containing carbon atoms ranging from 20 to 33. Paraffin wax is primarily used as a plasticizer in hot melt adhesives to adjust product viscosity and melt-rate. It is a major component in hot melt adhesives, especially in polyvinyl acetate (PVA) adhesives. Wax is also used in coating materials. The strong peak at 15.5 represents butylated hydroxytoluene (BHT), which is an antioxidant agent used in THF. Peak area of each identified peak is calculated to estimate the relative concentration of each component in the extracted stickies, and the estimated percentage are presented in Table 4. Paraffin wax is the predominant component in the stickies extracted from OCC, which makes up to 70.1% of total stickies. The percentage of polyamine, styrene, and resins in total stickies are 4.1%, 4.7% and 6.9%, respectively. Last, 14.7% of total stickies is a mixture of complex compounds which are difficult to identify, including high molecular weight esters and acids.

Table 3
GC-MS identified chemical compounds in solvent extracted stickies

Retention time (min)	Compounds	Peak area %
4.0	Dimethylamine	1.8
6.1	Dimethyl propylamine	2.3
7.6	Methylstyrene	4.7
10.4	Cyclotetrasiloxane	3.4
15.0	Cyclopentasiloxane	2.3
15.5	Butylated Hydroxytoluene	n.a.
24.1	Eicosane	0.9
24.9	Henecosane	2.5
25.6	Docosane	3.3
26.4	Tricosane	4.4
27.1	Tetracosane	6.5
27.8	Pentacosane	8.3
28.4	Hexacosane	9.1
29.1	Heptacosane	8.8
29.8	Octacosane	8.6
30.5	Nonacosane	6.8
31.4	Triacontane	5.0
32.4	Hentriacontane	3.6
33.6	Dotriacontane	2.4

Table 4
Chemical composition of stickies in OCC based on GC-MS results

Compounds	Potential origin	Percentage %
Polyamine	Paper additive	4.1
Styrene	Adhesive	4.7
Resin	Coating	6.9
Wax	Coating, adhesive	70.1
Others	Wood extractives, ink residues	14.2

Particle charge of dissolve and colloidal stickies

The water-soluble stickies typically contain a wide range of anionic dissolved materials, commonly known as anionic trash, or dissolved and colloidal substances (DCS). Some key components may include fatty acid salts, resin acid salts, hemicellulose and its oxidation byproducts, lignin derivatives from pulping, and dispersants or anionic latex and dispersants from coated broke. In addition, various types of bleaching agents tend to oxidize hemicellulose and extractives, further increasing the anionic charge of the dissolved and colloidal fraction of the pulp slurry. DCS not only interfere with the performance of cationic retention aids, cationic dry-strength agents, and wet-strength resins, but also play an important role in deposit problems. In this study, the dissolved charge as well as fiber charge were investigated using colloidal titration. The specific charge quantities of six recycled paper grades are shown in Table 5 below:

Table 5
Specific charge quantity of recycled fibers

	Recycled paper grades					
	Residential	OCC	Kraft Liner	Bleached Kraft	ONP	Mixed Office
Total charge of 0.1% fiber suspension (μeq/L)	4.51	4.37	4.19	3.52	2.01	1.86
Dissolved particles charge (μeq/L)	2.37	3.04	3.05	3.42	1.77	1.5
Fiber charge (μeq/g)	2.14	1.33	1.14	0.1	0.24	0.36

The results indicate that all recycled fibers and dissolved stickies carry negative charge. Among all grades, Residential possess the highest total charge of 4.51 μeq/L, followed by OCC containing 4.37 μeq/L total charge and Kraft liner containing 4.19 μeq/L total charge. Additionally, over 30% of the total charge in these three grades are contributed by fiber charge. Fibers derived from Residential contain 2.14 μeq negative charge per gram of dry fiber, which is the highest among all samples, followed by OCC fibers containing 1.33 μeq negative charge per gram of dry pulp, and Kraft liner fibers containing 1.14 μeq negative charge per gram of dry pulp. These results indicate that sticky contaminants heavily deposit on fiber surface and result in high negative charge.

Bleached kraft also has significantly high total charge. However, the contribution of fiber charge is minimal, which is significant less than that of Residential, OCC and Kraft liner fibers. On the other hand, the dissolved charge in Bleached kraft fibers is 3.42 μeq/L, which is the highest among all fibers. ONP and Mixed office, as the least contaminated recycled grades, contain 2.01 μeq/L and 1.86 μeq/L total charge, respectively. Similar to Bleached kraft, over 80% of the total charge in these two grades was contributed by dissolved particles. This may be due to the high amount of water-soluble ink substances in these cases.

Impact of sticky contaminants on paper product strength properties

Paper sheets were made using recycled fibers prior to solvent extraction (stickies retained) and recycled fibers post solvent extraction (stickies removed). The physical strength properties of these paper sheets were measured and compared in order to study the impact of the presence of sticky contaminants on paper products strength properties. The results are presented in Fig. 8(a)(b)(c). All sheets exhibit slightly increased physical strength as sticky contaminants were removed through solvent extraction. The most significant improvement is observed on OCC sheets, where tensile strength increased by 26% from 29.1 to 36.7, tear resistance increased by 53% from 2.3 to 1.5, and burst strength increased by 12% from 5.9 to 6.6. For Kraft liner sheets, tensile strength increased slightly from 43.1 to 44.5 (3%), tear index increased slightly from 7.4 to 7.9 (7%), and burst strength increased significantly from 2.8 to 3.3 (18%). Meanwhile, the tensile strength of Mixed office sheets increased by 11% from 51.4 to 57.0, the tear resistance increased slightly from 9.0 to 9.3 (3%), and the burst strength increased remarkably from 3.5 to 4.2 (20%). These results indicate that the removal of sticky contaminants can improve paper product physical strength properties, which is in agreement with previous research that the sticky contaminants in recycled fibers occupy accessible hydroxyl groups and reduce contacting areas, thus leads to reduction in paper physical strength (Douek et al., 2003).

Conclusions

The identification and characterization of sticky contaminants in recycled fibers indicates that these stickies vary in size, number and weight by different paper grades and their recovery methods. The majority of wastepaper grades collected from paper recycling mills contains 3–5 wt% stickies, while a curb side collected grade contains 15 wt% stickies. The average size of these stickies presented in recycled paper sheets is in the range between 0.004 to 0.012 mm^2 depending on the wastepaper grade. Additionally, the chemical analysis of THF extracted stickies by FT-IR and GC/MS provides evidence that the major components in the contaminants are polyvinyl acetate (PVA) polymers, styrene butadiene rubber (SBR), paraffin wax, resin, and polyamines. In addition, these stickies deposit heavily on fiber surface leading to high negative charge in fibers suspension ranging between 2 ~ 4.5 ueq/L. Furthermore, the removal of stickies by solvent extraction can improve the quality of recycled paper products indicated by comparing the physical strength properties of recycled paper sheets prior and after stickies extraction. SEM images explain that sticky contaminants cover fiber surface, reduce contacting areas, and occupy accessible hydroxyl groups, thus leads to reductions in paper strength. These findings will assist addressing the knowledge gaps in understanding the nature of stickies and their behaviors, and to eventually develop highly efficient technologies for contamination removal in the paper recycling process.

Declarations

Ethics approval and consent to participate

We confirm that this work is original and has not been published elsewhere, nor it is currently being considered for publication elsewhere. This manuscript represents the whole study, and we do not intent to split up this research to increase the quantity of submissions. All results are presented clearly and honestly without fabrication, falsification, or manipulation. All data, text or theories are the authors' own. All authors approve that this manuscript follow the Ethical Policy of the journal, and consent to participate any screening or investigation.

Consent for publication

All authors consent to submit this manuscript to the Journal of Cellulose for publication.

Availability of data and materials

All results, including data, figures, and tables are available for review or submission as supplement materials.

Competing interests

All authors have no relevant financial or non-financial interests to disclose.

Funding

This work is supported by REMADE Institute Projects and the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Manufacturing Office Award Number DE-EE0007897.

Authors' contributions

All authors contributed to the study conception and design. Material preparation, experimental investigation, data collection and analysis were performed by Yun Wang, Cornellius Marcello, and Neha Sawant. Funding acquisition and Resources were proved by Kecheng Li, Abdus Salam, Said Abubakr, and Dewei Qi. Supervision was provided by Kecheng Li and Abdus Salam. The first draft of the manuscript was written by Yun Wang and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Acknowledgements

All authors are grateful for the financial support provided by REMADE Institute Projects and the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Manufacturing Office Award Number DE-EE0007897.

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Figures

Figure 1

Recycled paper raw materials collected from local paper mill.

Figure 2

Examples of visible sticky contaminants on wastepapers.

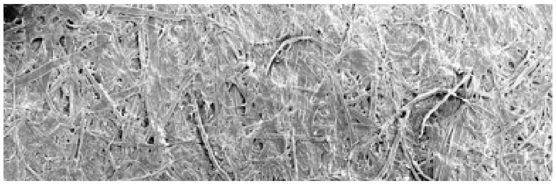


Figure 3

SEM images of adhesive contaminants on recycled OCC, (a) control sample 40X, (b) adhesive contaminants 40X, and (c) enlarged adhesive contaminants 300X.

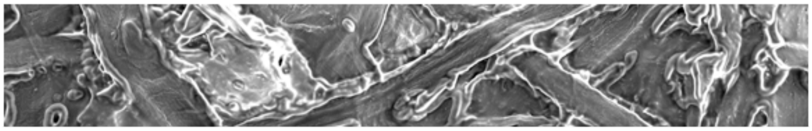


Figure 4

SEM images of sticky contaminants on Residential Wastepaper at different magnification levels, (a) 200X, (b) 500X.

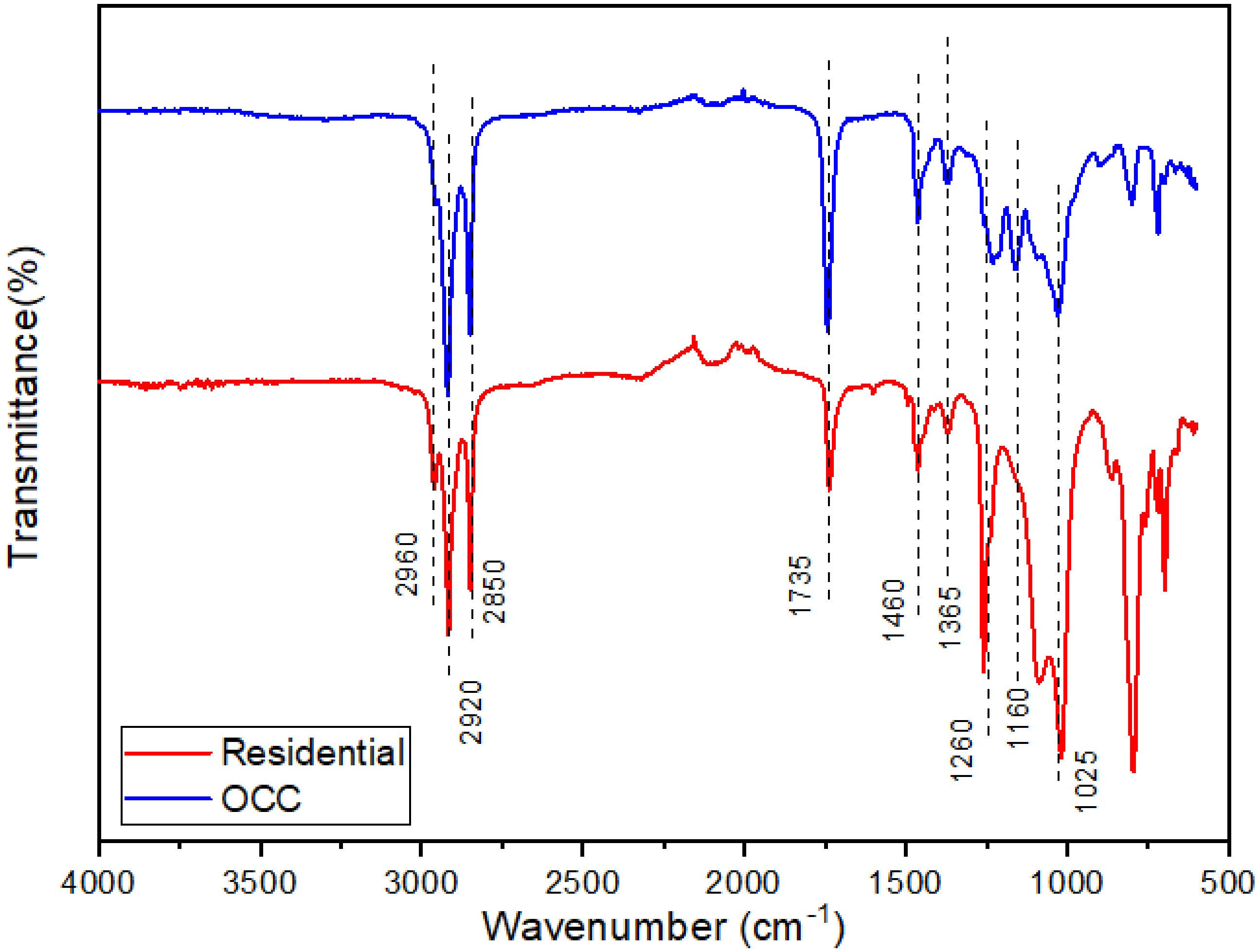


Figure 5

FT-IR spectrum of THF extracted stickies from OCC and Residential, respectively.

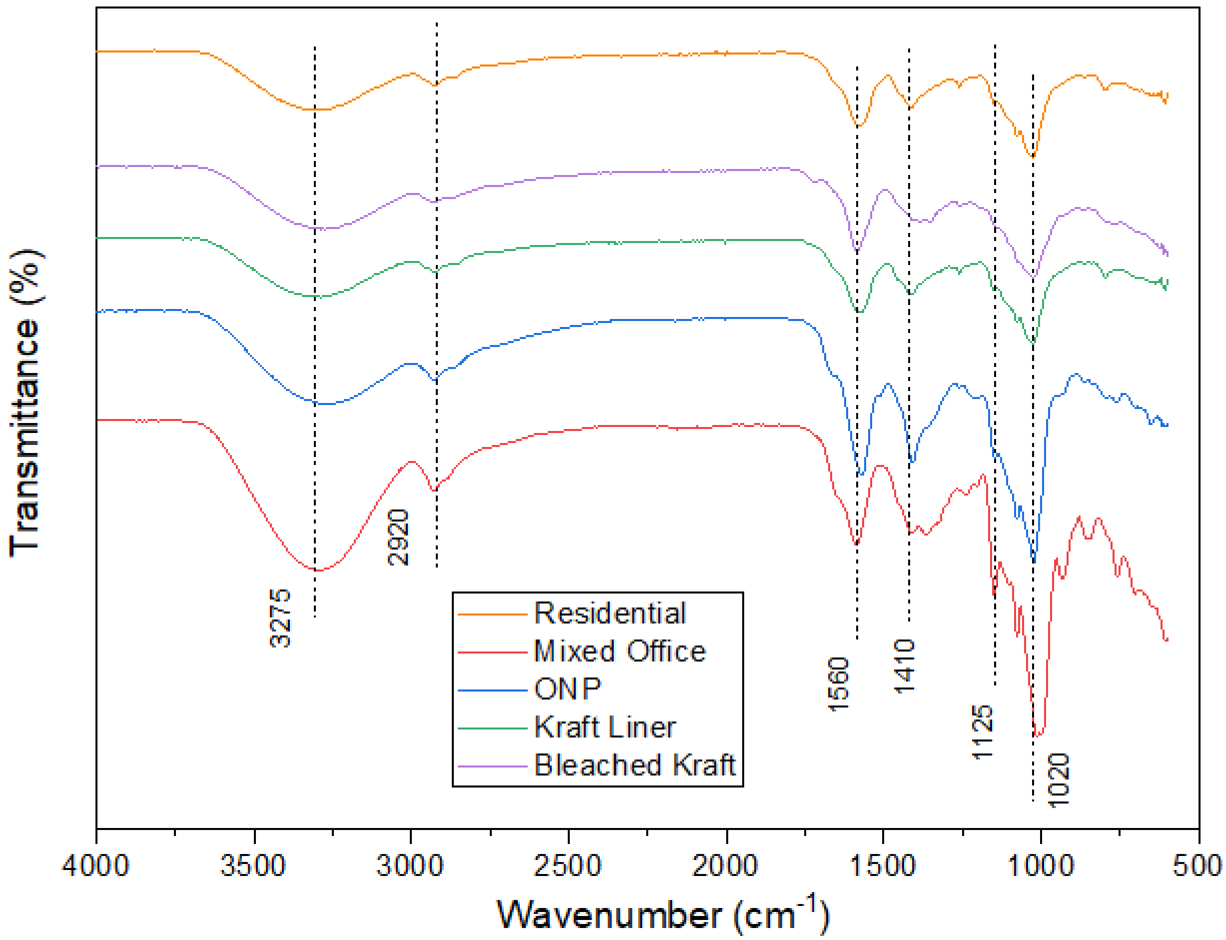


Figure 6

FT-IR spectrum of water extracted stickies from Residential, Mixed Office, ONP, Kraft Liner, and Bleached Kraft, respectively.

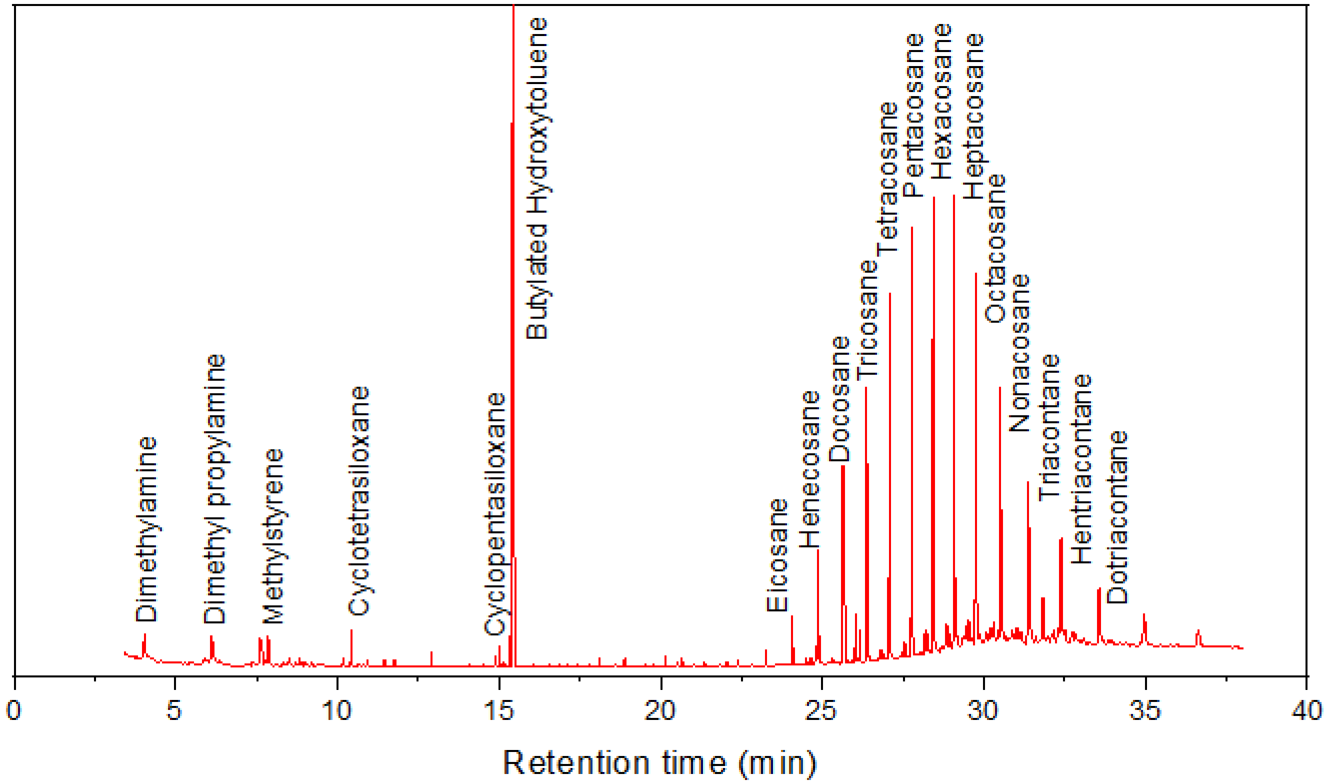
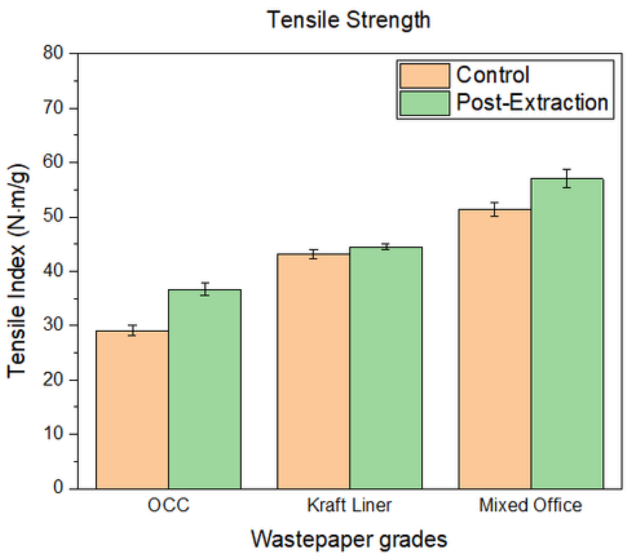


Figure 7

GC-MS spectrum of stickies extracted from OCC.



(a)

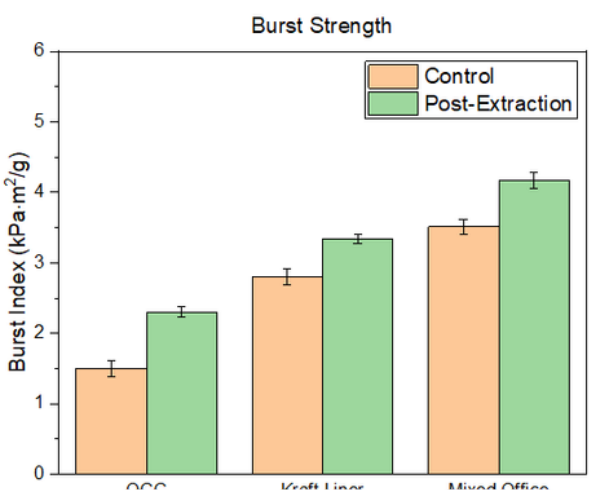


Figure 8

Physical strength properties of recycled paper sheets. (a) tensile strength, (b) burst strength, and (c) tear resistance.