

IDENTIFICATION OF THE ORIGINS OF STICKIES IN DEINKED PULP

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THIS STUDY IDENTIFIES THE DIFFERENT TYPES OF STICKIES FOUND IN RECYCLED PAPER AND CORRELATES THEM TO THEIR ORIGINS IN THE MIXED OFFICE WASTE THAT IS TYPICALLY USED TO PRODUCE RECYCLED PAPER.

THE PRESENCE OF STICKY CONTAMINANTS (STICKIES) in the reclaimed-fiber furnish is one of the major problems in producing quality recycled papers. The problem is even more severe when recycling mixed office waste (MOW), especially when the MOW contains assorted mixtures of file folders with adhesive labels, address labels, polymer coated printed matters, etc., in addition to white ledgers (1). Many workers have discussed methods of overcoming the stickies problem (2-4) and the techniques for measuring stickies (5). Others have described the various polymers used in adhesives, inks, coatings, binders, etc., as potential sources of stickies in the deinked pulp (6). However, there has been no discussion with respect to identifying the exact origins of the stickies found in the deinked pulp.

The object of the present work was to establish the chemical identity of stickies found in white-grade recycled pulp and to link these findings with the chemistry of adhesive materials in the MOW used to produce the recycled pulp. Identifications were made using Fourier-transform infrared spectroscopy (FTIR) with special accessories. The analyses enabled us to identify the chemistry of the stickies and connect them with their origins.

EXPERIMENTAL

Potential stickies in MOW

Various types of adhesive materials (potential stickies) were present in a MOW recycle mill warehouse. Four different items were chosen, since they were abundantly present in the recovered paper bales:

- Tax-document envelope
- Sales-lead label
- File folder
- Address label.

Deinked-pulp stickies

Pulp slurry samples were collected from two points of the deinking-recycling process: after chlorine bleaching and after the fine screen before flotation. The pulp samples from both locations were passed through a 0.006-in. (152 μ m) vibrating screen. Stickies collected on the screen were transferred onto filter paper and dried in a press. The filter papers containing stickies were labeled as follows:

- F1: stickies collected after chlorine bleaching
- F2: stickies collected after the fine screen before flotation.

FTIR analysis

Fourier-transform infrared spectroscopy (FTIR) analysis was used to identify stickies. A spectrometer (Bio-Rad Digilab® FTS 60-A) with an ATR (attenuated total reflectance) attachment (Harrick Scientific SplitPea® Micro ATR) was used to analyze the potential stickies in the recovered paper. Another spectrometer (Bio-Lab Digilab FTS 40) with an IR (infrared) microscope (Digilab UMA300) was used to analyze the stickies collected on filter papers F1 and F2.

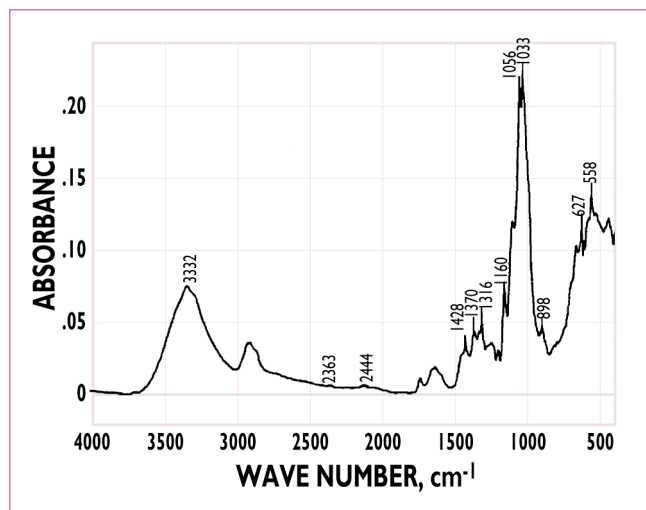
Extraction of recovered paper with water

The recovered paper samples were also extracted with water to identify the water-soluble adhesives. Analysis of the water extracts was carried out after drying on a Zn-Se plate as a film. The spectra of these films were obtained with the FTS 60-A spectrometer.

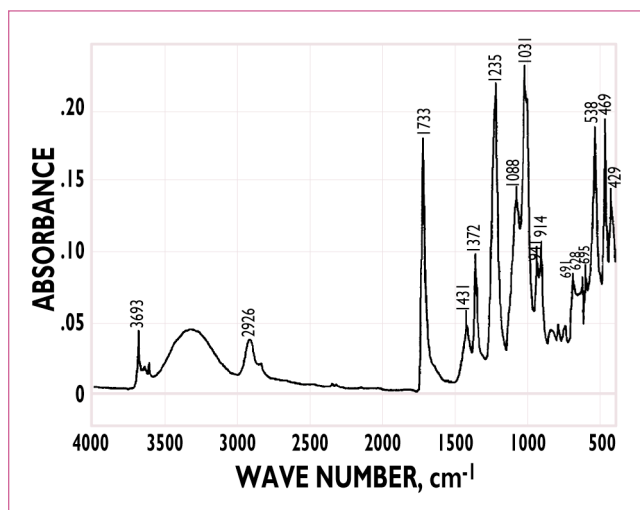
RESULTS AND DISCUSSION

FTIR analysis of potential stickies

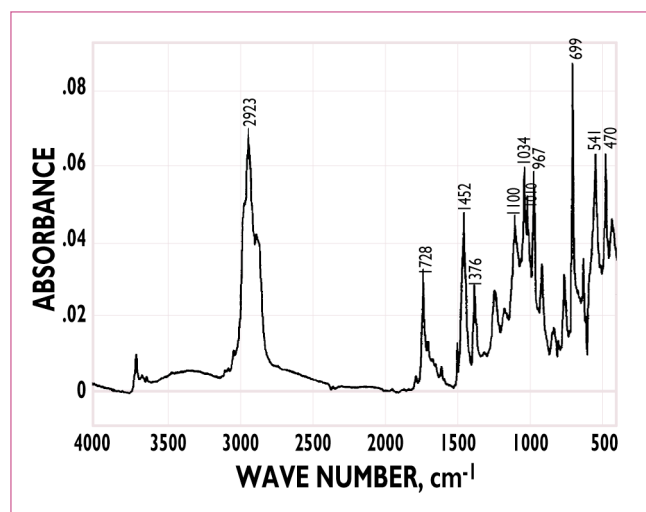
The chemical structures of the various potential stickies from the MOW were determined by FTIR, as described by the following:



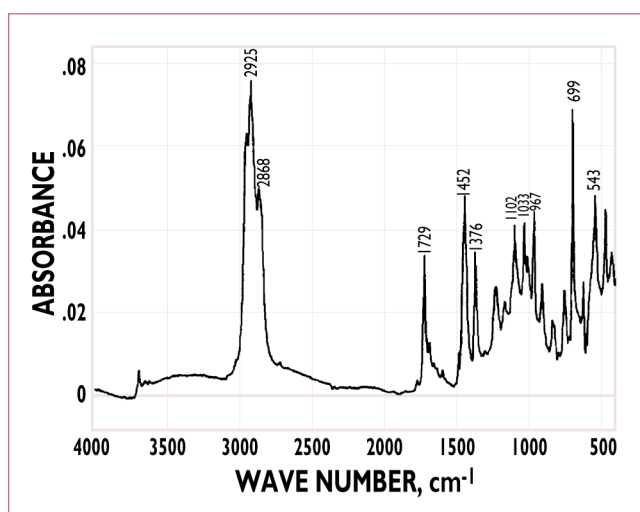
1. FTIR spectrum of tax-document envelope window



2. FTIR spectrum of tax-document envelope adhesive



3. FTIR spectrum of label adhesive between label and paper



4. FTIR spectrum of label adhesive between label and glossy paper

Tax-document envelope. Envelope window: cellulose with some additives, as evidenced by the FTIR spectrum in Fig. 1. Envelope adhesive: poly(vinyl acetate) (Fig. 2). This was a green adhesive (activated by wetting with water) for sealing the envelope.

Sales-lead label. Adhesive between label and paper: mainly hydrocarbon, with mono and para substituted aromatics (Fig. 3). Adhesive between label and glossy paper: same as adhesive between label and paper (Fig. 4).

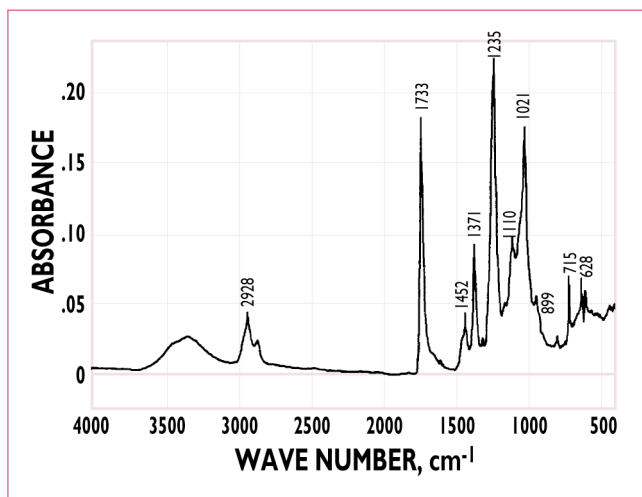
File folder. Adhesive between tab fold of file folder: poly(vinyl acetate) (Fig. 5). Adhesive under color-coded label: very similar to Sales-lead Label adhesive between label and paper (Fig. 6). Adhesive under clip-bearing tape: EVA (copolymer of ethylene and vinyl acetate, 85/15), similar to the hot-melt adhesive used in our study

on the removal of stickies with flotation aids (3) (Fig. 7). Clip-bearing tape: tape is made of polyester fiber (Fig. 8).

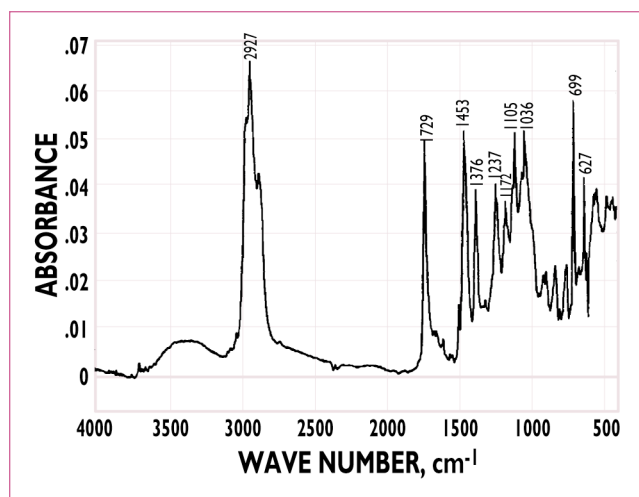
Address label. Pressure-sensitive adhesive label: poly(2-ethylhexyl acrylate) (Fig. 9).

FTIR analysis of water extracts of potential stickies
Several of the MOW samples were soaked in water to extract any potential water-soluble stickies. As expected, FTIR revealed the presence of starch in all samples. The following samples had other water-soluble components:

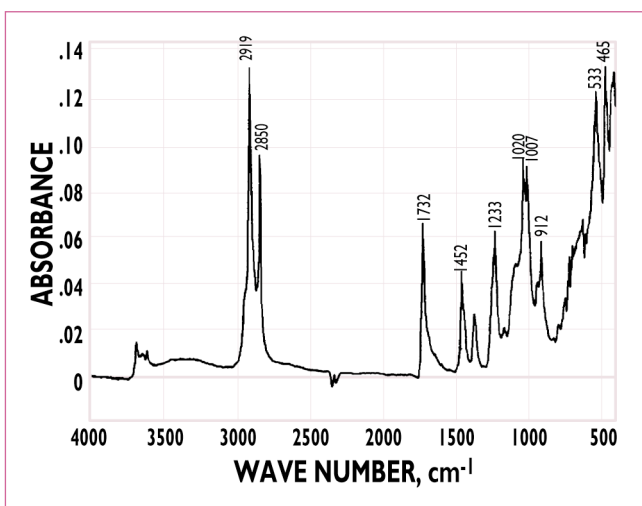
Tax-document envelope. The green adhesive contained acetate ester and an amide or carboxylic acid car-



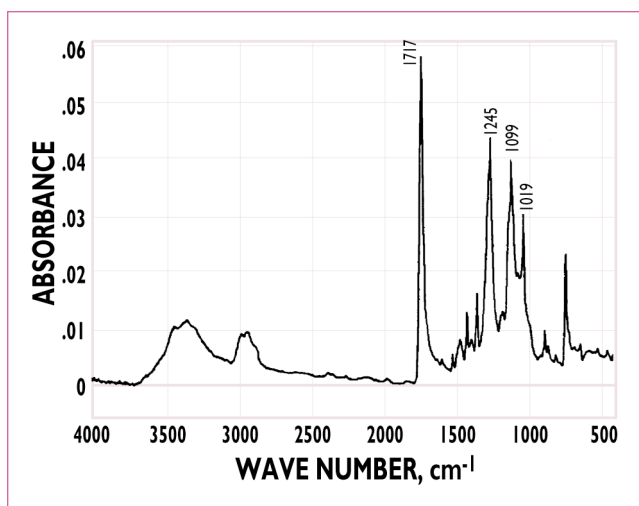
5. FTIR spectrum of file folder adhesive between tab fold



6. FTIR spectrum of file folder adhesive under color label



7. FTIR spectrum of file folder adhesive under clip-bearing tape



8. FTIR spectrum of file folder clip-bearing tape

bonyl.

Sales-lead label. The label adhesive contained starch and a small amount of carbonyl at 1730 cm^{-1} , which could indicate an acid carbonyl.

File folder. The tab adhesive contained starch and a small amount of carbonyl at 1730 cm^{-1} , which could be an acetate ester carbonyl. Analysis of the adhesive on the color-coded labels showed carbonyl between 1717 cm^{-1} and 1700 cm^{-1} , which could be acids or ketones or both. The adhesive on the clip-bearing tape contained starch and showed a very intense and broad carbonyl band centering at 1700 cm^{-1} and an intense O-H stretch, indicating the presence of either alcoholic or acid OH group.

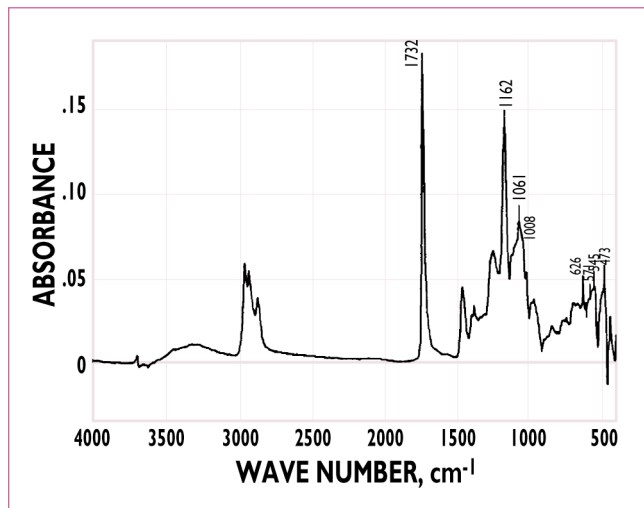
FTIR analysis of stickies on filter pads

Filter pad 1. Four stickies on filter pad 1 (F1, stickies

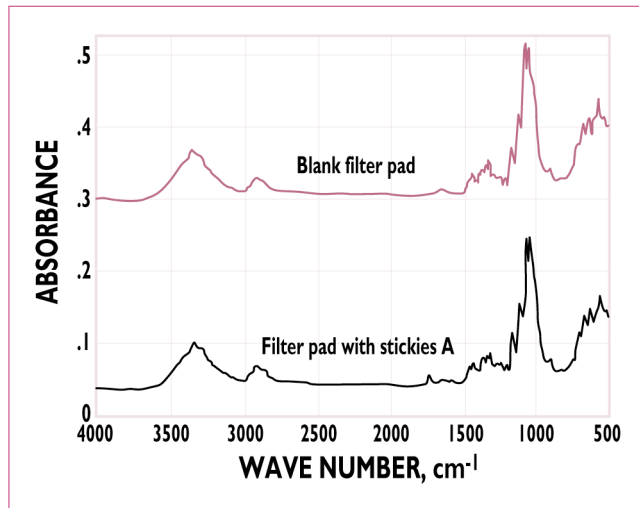
collected after chlorine bleaching) were examined using a spectrometer with the Split Pea ATR attachment. The difference spectra for the stickies—obtained by subtracting the background spectrum of the filter pad from the spectrum of the stickies—were examined.

Figure 10 shows two FTIR spectra: one for the blank filter pad (top), and one for a filter pad with stickies (bottom). **Figure 11** shows an example of a difference spectrum, where the difference spectrum for the stickies is obtained by subtracting the spectrum for the blank pad from that of the pad with stickies. Analysis of the difference spectra for the four stickies on pad F1 revealed the following:

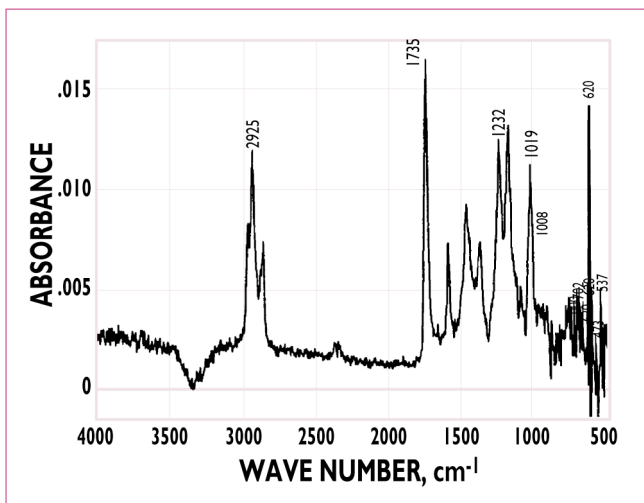
Stickies A (F1-A): This was a vinyl acetate/acrylate copolymer, probably with a very minor amount of car-



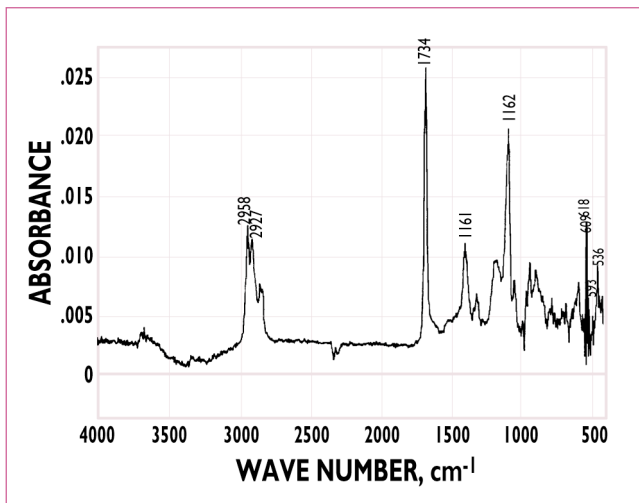
9. FTIR spectrum of address label pressure-sensitive adhesive



10. FTIR spectra of blank filter pad (top) and filter pad containing stickies (bottom)



11. FTIR difference spectrum for pad F1, stickies A (F1-A)



12. FTIR difference spectrum for pad F1, stickies B (F1-B)

boxylic acid monomer. The acrylate monomer appeared to be 2-ethylhexyl acrylate (2EHA) because of the presence of long-chain (octyl) aliphatic bands in the IR spectrum (Fig. 11). The monomer 2EHA is very commonly used in production of polymers with low glass-transition temperatures (T_g) (latex for coatings and nonwoven bindings; UV coating, ink, or adhesive formulations; etc.), where softness or tackiness is required (7).

Stickies B (F1-B): This was mainly poly(2-ethylhexyl acrylate) (Fig. 12).

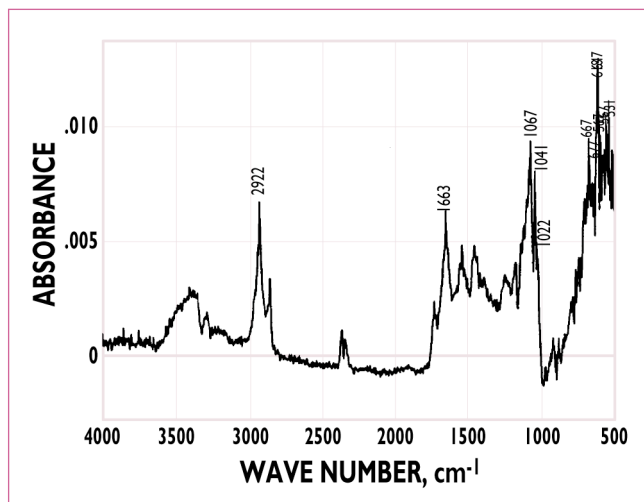
Stickies C (F1-C): The spectrum showed the presence of substituted amide, aliphatics, and ester (Fig. 13). The stickies material could be an acrylic ester latex polymer

made with n-methylolacrylamide (a crosslinking monomer). The monomer n-methylolacrylamide can crosslink with cellulosic hydroxyl.

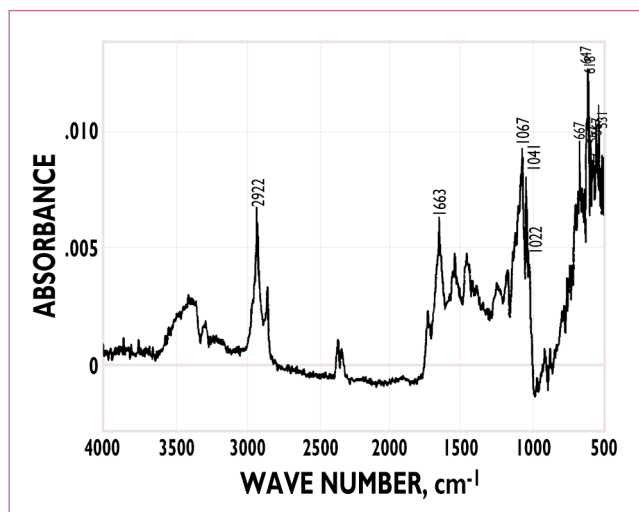
Stickies D (F1-D): The spectrum shows carboxylate, aliphatics, and possibly nitrate (Fig. 14). This material could be a water-soluble carboxylic acid-containing polymer.

Filter pad 2. Analysis of the difference spectra for the three stickies on filter pad 2 (F2, stickies collected after the fine screen before flotation) revealed the following:

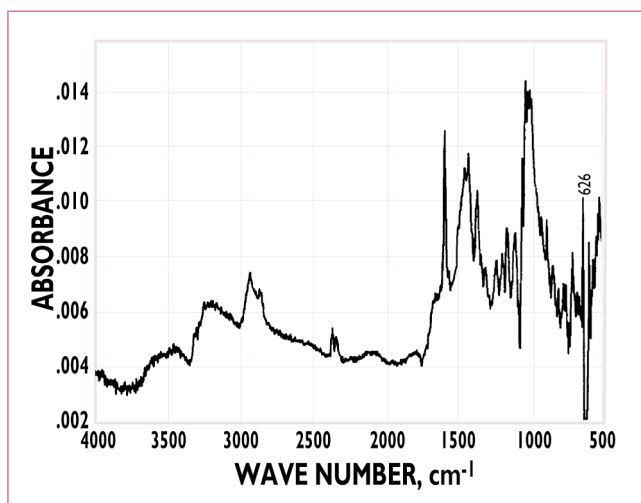
Stickies A (F2-A1 and F2-A2): This stickies spot showed two distinctively different color areas, which were examined separately and gave different polymer



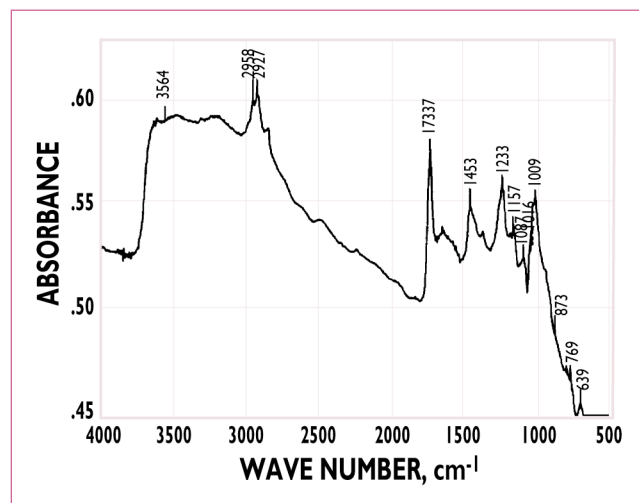
13. FTIR difference spectrum for pad F1, stickies C (F1-C)



14. FTIR difference spectrum for pad F1, stickies D (F1-D)



15. FTIR difference spectrum for pad F2, stickies A1 (F2-A1)



16. FTIR difference spectrum for pad F2, stickies A2 (F2-A2)

compositions. F2-A1 (Fig. 15) showed very similar composition to F1-D and indicated the presence of some carbonate. The carbonate is probably from calcium carbonate, which was found in the pressure-sensitive adhesive label that was used for our study (3). F2-A2 (Fig. 16) showed predominantly poly(vinyl acetate) with some 2EHA, which is somewhat similar to F1-A.

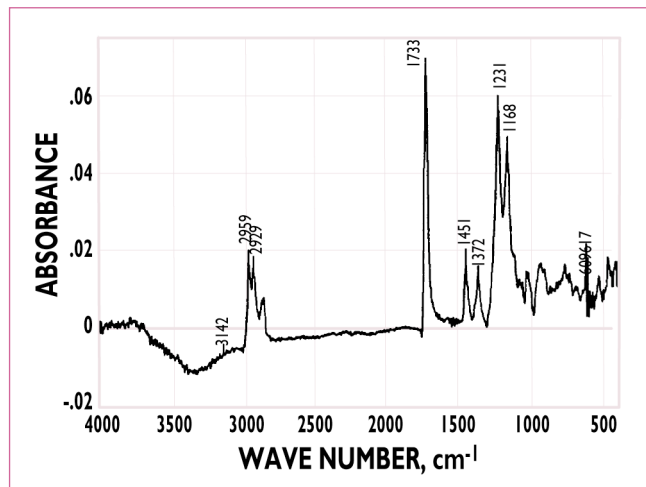
Stickies B (F2-B): This sample was a copolymer of vinyl acetate and 2EHA (Fig. 17), which is similar to F2-A2 but with much higher content of 2EHA, making it more tacky at room temperature.

Stickies C (F2-C): This sample was almost identical to F2-B, a copolymer of vinyl acetate and 2EHA (Fig. 18).

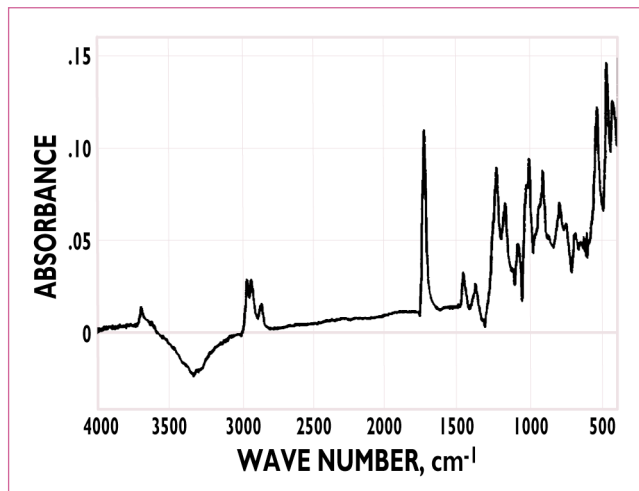
CONCLUSIONS

The results presented here clearly indicate that some of these “potential stickies,” such as the adhesives from the file folder and tax-document envelope, are water soluble. Most likely, they are composed of polymers made with carboxylic acid monomers, such as acrylic acid, or a polymer that could become water soluble through hydrolysis, such as poly(vinyl acetate).

Examination of the filter pads appeared to indicate that some carboxylates were present in some stickies spots. However, the amount was insufficient for us to isolate for further tests (solubility in alkaline water) to determine if they were agglomerated micro stickies. The FTIR examination of the “potential stickies” from the MOW samples showed that the adhesives mainly consisted of



17. FTIR difference spectrum for pad F2, stickies B (F2-B)



18. FTIR difference spectrum for pad F2, stickies C (F2-C)

polyacrylates and homo- or copolymers of vinyl acetate. It is well known that 2-ethylhexyl acrylate is the major monomer used to produce low- T_g polymers with the tackiness required in pressure-sensitive adhesives.

By comparing the interpretation of FTIR spectra, it is possible to associate stickies found on the filter pad to the origins of stickies from the MOW. For example, Stickies B from the chlorine bleaching accept filter pad (F1) could have originated from the address label, since FTIR showed that both were poly(2-ethylhexyl acrylate). However, some stickies found on the filter pad showed the presence of both polyacrylate and poly(vinyl acetate). This material was more complex but could be interpreted as either a copolymer of vinyl acetate and acrylate or as the agglomeration of different stickies during the deinking process. Stickies A from the fine-screen accept filter pad (F2) could be the cause of agglomeration of partially hydrolyzed vinyl acetate copolymer or other water-soluble polymers.

Although the recovered paper bales were not sorted to isolate and quantify the amounts of various potential stickies, the comparison of the FTIR analyses of the materials found in the recovered paper and the stickies on the filter pads clearly showed that they are related. The results also showed that polyacrylate adhesives were the major culprit in the sticky contaminants. Furthermore, poly(2-ethylhexyl acrylate)—valued as an adhesive component for its ability to remain tacky at low temperature—is the most troublesome stickies material found in many samples. **TJ**

Hsu, principal scientist/project leader, Schroeck, technical service representative, and Errigo, technical application associate, work in the Fiber Recycling Group, Paper Chemicals Dept., Cytec Industries Inc., Stamford, CT 06904-0060.

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