

DEVELOPMENT OF NEW METHODS FOR CHARACTERIZING UNIFORMITY OF YANKEE COATINGS

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ABSTRACT

An adhesive coating formed on the surface of a Yankee dryer is critical for manufacturing creped tissue and towel grades. Due to the complexity and dynamic nature of the creping process, there has been very limited information available on the structure of Yankee coatings. This paper discusses laboratory methods for preparing Yankee coating films and imaging techniques, atomic force microscopy (AFM) and scanning electron microscopy (SEM) that were used to characterize these films. The effects of various modifying agents are demonstrated on the structural and compositional uniformity of the Yankee coating films. The applicability of the SEM and AFM data from this study to the actual creping process and the practical aspects of the results are also discussed.

INTRODUCTION

The defining properties of tissue, including softness, bulk, stretch and absorbency, are for the most part achieved by creping the tissue with a doctor

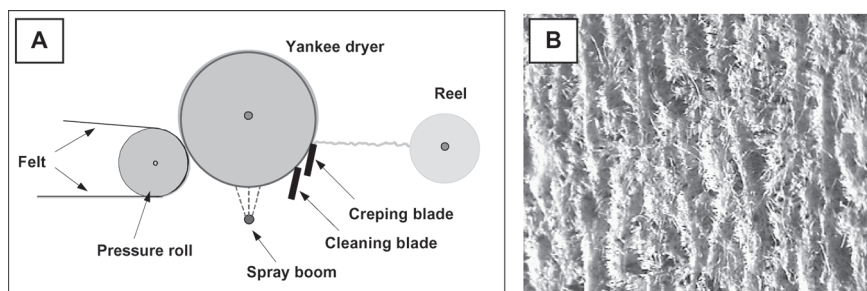


Figure 1 (A) Creping operation. The wet fiber web, carried by a felt or a fabric, is largely dewatered at the pressure roll. At the pressure roll nip, the sheet is transferred to the Yankee dryer surface, which has been sprayed with an adhesive. At this point the paper web has a consistency of 40–80%. The sheet and the adhesive layer are further dried on the hot (90–150°C) Yankee dryer to 90–98% consistency. The adhesion between the sheet and the Yankee dryer coating is developed during drying. The sheet is removed with a doctor blade producing a sheet with creped structure. (B) Microphotograph at a 40× magnification of a creped tissue sheet.

blade after it has been dried on a steam-heated Yankee dryer cylinder. The diagram in Figure 1A shows a simplified Yankee dryer operation. The mechanical action of the creping blade results in a disruption of the fiber-fiber bonds and formation of a micro-fold structure within the sheet [1, 2]. These microfolds are called crepes and the process is referred to as creping.

In order to develop the crepe, the paper web has to adhere to the surface of the Yankee dryer. Adhesion is provided by spraying an adhesive on the dryer. The most common Yankee adhesives are synthetic polymers such as polyaminoamides, polyamines, polyvinyl alcohols, polyvinyl acetates and polyethers. The predominant chemistry uses polyaminoamides crosslinked with epichlorohydrin (PAE). The creping process and the chemistry of the Yankee adhesives have been previously reviewed [2–7].

Release oils are traditionally used to alter the Yankee adhesive properties, primarily to decrease adhesion and release the sheet from the dryer at the creping blade. Typically, the adhesive and the release oil are applied to the Yankee dryer, being mixed together and diluted to approx. 1 wt.% actives or less, by spraying through a spray boom. Upon rapid evaporation of water on the hot Yankee dryer surface, the adhesive/release oil blend forms a tacky Yankee coating. An emulsifying surfactant package is often formulated into release oil products to disperse the oil in the water medium. However, even with these emulsifying surfactants, the hydrophobic release oils are not

miscible with water-soluble PAE-type adhesives. This should have a detrimental effect on the uniformity of Yankee coatings.

A common industry belief is that release oil migrates from the hot Yankee dryer surface towards the air side creating a gradient of the release oil concentration within the Yankee coating [4–6]. Thus, the outer layers (airside) primarily consist of oil that helps lubricate the creping blade. The coating layers, that are closest to the dryer side, are composed of a completely cured adhesive with no release oil, which makes them very hard. The middle section of the coating contains emulsified oil that softens the adhesive. To the best of our knowledge, no experimental evidence has been reported to support this concept. In recent years, more compatible modifying agents, e.g., surfactants and humectants, have been introduced as alternatives to release oils. These modifying agents are the subjects of current research and commercial interest [8, 9].

A superior Yankee coating should form a uniform film that will provide good adhesion for efficient drying and creping of the tissue. The coating uniformity is critical not only for consistent creping that affects the quality of the produced sheet, but also for even coverage of the Yankee surface to prevent the cylinder and the blade from premature wear. Despite the wide variety of chemistries and products offered on the market, very limited scientific data is available concerning the effect of modifying and release agents on the uniformity of the Yankee adhesive films. Much earlier work sought to help define the structure of Yankee coatings formed from natural furnish components such as hemicellulose [10–12].

This paper presents the first published attempt at structural elucidation of Yankee coatings formed from synthetic additives. Laboratory methods were developed for preparing the Yankee coating films, which were studied using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

EXPERIMENTAL

Materials

The creping aids used for making Yankee coating films were commercial products available from Nalco Company (Naperville, IL, USA). Abbreviations given to the products and their general chemistries are described in Table 1. The adhesive was a 15-wt.% aqueous solution of polyaminoamide crosslinked with epichlorohydrin (PAE). For equal comparisons, all the films were made with additives at two add-on levels, 5 and 20 wt.%, based on the PAE polymer.

Table 1 Description of products used for making films.

Product	Chemistry
PAE	Poly(aminoamide) cross-linked with epichlorohydrin, 15 wt.% aqueous solution
RO	Release oil product containing hydrocarbon oil and non-ionic surfactants
M1	Blend of 75% cationic surfactant and 25% non-ionic surfactant
M2	Non-ionic surfactant
M3	Proprietary polyol humectant
M4	Inorganic phosphate salt

Film preparations

Two techniques were used for making Yankee coating films for these studies. The first technique involved casting a film by slow drying an aqueous solution of PAE or its blend with the release oil or a modifier. These samples were placed in a mold and heated in an oven at 90°C for 14 hrs. The formed films were further dried in a vacuum oven at 110°C to constant weight and stored in a desiccator. The thickness of the resultant films was 0.4–0.6 mm.

The second technique employed casting of thin films by spin coating on a substrate, either mica or cast iron. A single wafer spin processor (WS-400A-6NPP/Lite, Laurell Technologies, North Wales, PA) was used with custom-made chucks.

Films on mica were made using mica sheets that were split just prior to coating them in order to obtain a fresh surface. The samples were applied to the mica at room temperature. A 1-ml product sample was applied to the center of the mica sheet in the beginning of a spin cycle (Table 2). The films were dried in an oven at 150°C for 30 min. The films were then quickly cooled under liquid nitrogen for 10 s in order to minimize structural changes the films might undergo during a transition from a melt to a solid state. The resultant specimens were stored in a desiccator prior to imaging.

Films prepared on a cast iron surface were made using cast iron (grade GCCL-40) coupons that were embedded into the top of phenolic resin disks. The cast iron surface was then mirror-polished, rinsed with water and isopropanol and air-dried. The same spin program (Table 2) was used as for the films on mica. The adhesive samples were applied to a hot cast iron surface. The disks were preheated to 150°C and the product samples were preheated to 50°C. During the spin cycle the temperature of the coated surface dropped

Table 2 Spin program used for casting Yankee coating films on mica or cast iron.

Step	Speed (rpm)	Time (s)
1	500	5
2	2000	5
3	6000	15

to 90–105°C. After the spin cycle was finished, the coated disks were immediately placed in an oven to dry for 30 min at 150°C. The dried films were cooled in liquid nitrogen for 60 s. The samples were stored in a desiccator prior to imaging.

For multilayer films on the cast iron surface, the procedure described above was repeated five times. A new coating layer was applied after each drying stage. The temperature of the disk and the film remained above 90°C during all five spin cycles. After the fifth layer was dried, the film was cooled under liquid nitrogen for 60 s and stored in a desiccator.

SEM Imaging

A scanning electron microscope (SEM), Cambridge 360, was used, which is a standard tungsten filament, high vacuum microscope. The SEM was equipped with a four-quadrant backscatter electron detector that can provide both topographical and atomic contrast information. An Energy-dispersive X-ray Spectrometer (EDS), Thermo-Noran, Vantage II, was used to provide specific elemental composition from selected surface portions of a sample.

Characterization of a prepared specimen with the SEM required mounting each specimen as either the flat external surface of the coating or as a fractured, cross-sectional, orientation of the coating material. For obtaining cross-sectional images of the films prepared by slow evaporation, the films were fractured after freezing in liquid nitrogen. The film fragments were mounted to a ‘level’ position by vertically placing a piece of the film, with the opposite edge down, into a dollop of melted glue on the mounting stub. Films formed on mica sheets were mounted directly onto a specimen stub, external coating up, using a conductive graphite tape to secure the specimen. In both cases, continuity from either the mica sheet edge or from the fractured edge to the mounting stub was provided by application of carbon paint. The multilayer films prepared on cast iron were fractured after freezing with liquid nitrogen. The small coating sections were selectively dislodged with a fine needle probe. Each section was mounted vertically onto a specimen stub

using a conductive (graphite) tape to secure the specimen. The applied Au/Pd coating provided continuity from the fracture edge of the coating to the mounting stub.

Imaging to reveal the general morphology of each specimen was done utilizing the backscatter electron detector in the topographical mode (BEIt). Generally, all BEIt images were taken of a sample specimen after sputter coating with 20 nm of Au/Pd metal. Images in BEIt mode were taken using 8.0 kV excitation voltage, at a probe current of ~300 pA and a nominal working distance of ~10 mm. The top two quadrants of the backscatter detector were inverted to produce a topographical image. Imaging to reveal any detectable changes in surface elemental composition was done utilizing the backscatter electron detector in atomic contrast mode (BEIac). All BEIac images were taken of a sample specimen after evaporating a nominal 50-nm layer of graphite on the specimen surface. Images in BEIac mode were taken using 10.0 kV excitation voltage, at a probe current of ~300 pA and a nominal working distance of ~10 mm.

AFM Imaging

The AFM images of the films were obtained at room temperature using an atomic force microscope (Dimension 3100, Digital Instruments, Santa Barbara, CA). In order to avoid damaging the surface of the relatively soft adhesive films, imaging was carried out in the TappingMode™ regime. In this regime, the AFM operates by scanning a silicon probe tip attached to the end of oscillating cantilever at its resonance frequency across the sample surface. The intermittent contact cantilevers, model BS-Tap300A1, were purchased from Nanoscience Instruments (Phoenix, AZ). Height, amplitude and phase images were simultaneously collected. A third order plane fitting technique was applied to the height images in order to correct for distortions due to the tilting effect of the piezo tube. A more detailed description of the AFM method can be found in [13, 14]. The surface roughness was calculated from the height images using the root mean square average of height deviations from the mean data plane (RMS value). It was very important to store the film samples in a desiccator to prevent the film from picking up moisture. Moisture had a dramatic affect on the adhesion properties of the Yankee coating films. Even after drying, the films with some of the additives were tacky enough to cause an interference with the normal oscillation of the cantilever, which affected the image quality.

DSC Measurements

A TA 2920 differential scanning calorimeter (TA Instruments, New Castle, DE) was used to measure the glass transition temperature of the polymers. A film of the sample was cast at 105°C. The glass transition temperature (T_g) of the polymer was determined from the second scan by using a half-height method.

RESULTS AND DISCUSSION

In order to study uniformity of the Yankee coatings in the laboratory, several film casting techniques were developed. Ideally, to simulate the actual process on the Yankee dryer, the adhesive films would have to be prepared by using 1-wt.% aqueous solutions of the adhesive blends, and these would continuously be sprayed on a hot (90–150°C) cast iron surface. Although not impossible, it would be very difficult to study films made in this fashion due to macroscopic non-uniformities that could result from uneven coverage and entrapped bubbles. Therefore, various other approaches were explored.

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to study the Yankee coating films. SEM is a powerful method that has become the main tool for visualization of the morphological and topographical structure of various materials [15]. SEM was used to study both the surface and cross-sections of the films. The Energy-Dispersive Spectrometer (EDS) capabilities of the SEM also allowed us to characterize the elemental composition of the selected surface portions of the films. The disadvantage of this method is that SEM does not give high contrast images on flat samples, requires a vacuum and often demands substantial sample preparation.

Atomic Force Microscopy can be an alternative or complimentary technique to SEM. AFM is a non-destructive method that provides a very high three-dimensional spatial resolution and, unlike other traditional microscopy techniques, allows quantification of the surface roughness or other spatial features. AFM images provide unambiguous information about topography, showing which feature is higher or lower. Also, there is no mixing-in of buried sample layers into the measured image. AFM requires little to no sample preparation and can be used under ambient conditions. The main disadvantages, however, are a slow acquisition speed, a limited Z-height, typically 4 μm , and a limited scan range, typically 100 μm . Nonetheless, AFM is becoming increasingly important in material characterization, including polymer and paper studies, with regard to both surface topography and surface mechanical properties [16–19].

Films prepared by slow drying

The most straightforward method was to dry the adhesive in a non-stick mold having a flat surface (see Experimental section). The PAE adhesive film obtained using this method was clear. The films were fractured after freezing in liquid nitrogen and the SEM images were taken of the cross-sections. In order to make a thick film free of entrained bubbles, the drying temperatures had to be held below 100°C, which made the process very slow. This was not a problem for the PAE film with no additives or containing compatible modifiers (e.g., humectant, M3), but with less compatible release oil (RO) or surfactant-type modifiers, M1 and M2, phase separation was an issue. The temperature selected for making these films was 90°C. At this temperature there were no bubbles formed in the PAE films as evident from the SEM image of the film cross-section (Figure 2A).

At a 20 wt.% concentration of RO, M1 or M2, the Yankee coating films exhibited significant phase separation that occurred over the course of drying, while the PAE films containing the humectant, M3, or the inorganic phosphate, M4, provided visually uniform films. With 5 wt.% of release oil, the film appeared to be opaque, but uniform; while, films with 5 wt.% surfactant, M1 or M2, had clear areas and dark spots distributed in the film.

As discussed above, release and modifying agents are used to alter properties of the Yankee coatings, for example, adhesion and glass transition temperature (T_g). The latter was previously shown to be a good indicator of compatibility of additives with the PAE polymer [8]. Table 3 includes the T_g data for the PAE films containing additives used in these studies.

Table 3 The effect of release oil and modifiers on the glass transition temperature (T_g) of the PAE adhesive films.

Additive	T_g^1 (°C)	
	5 wt.% additive	20 wt.% additive
None	85 ²	—
RO	90	89
M1	86	86
M2	87	82
M3	62	34
M4	77	76

¹Measured by DSC technique

²PAE without additives

The T_g data were further correlated with the uniformity of the films characterized by the SEM technique. Blends of the PAE and the release oil product resulted in non-uniform films containing emulsified droplets of oil within the PAE matrix (Figure 2B). Release oil had no significant effect on the polymer T_g within the experimental error. The surfactants, M1 and M2, also had no effect on the T_g , which was again consistent with non-uniformity of the films modified with these additives (Figure 2C-D). In contrast, the polyol humectant, M3, that formed clear and uniform films with PAE (Figure 2E), appeared to be an effective plasticizer, significantly lowering the T_g of the PAE polymer. Such an effect on the T_g indicates attractive interactions between the M3 molecules and the PAE polymer. Finally, the phosphate, M4,

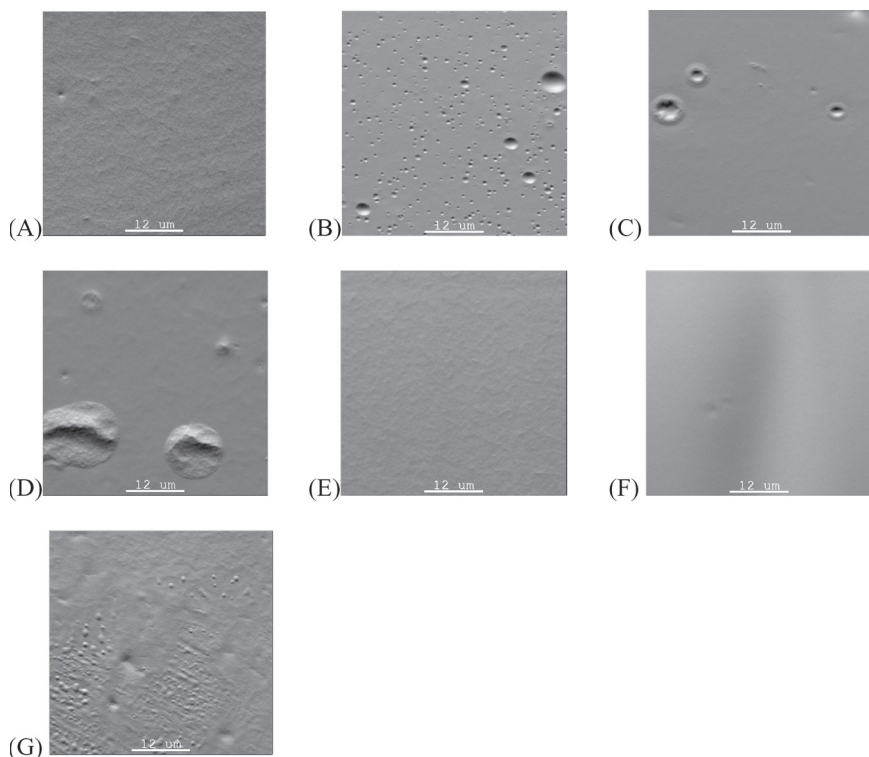


Figure 2 SEM (BEIt) images of cross-sections of the PAE adhesive films obtained by the slow drying technique: (A) no additives, (B) 5% RO, (C) 5% M1, (D) 5% M2, (E) 5% M3, (F) 5% M4 and (G) 20% M4. Magnification at 2000 \times .

produced a clear PAE film at a 5 wt.% concentration and resulted in a lower T_g . However, an increase of the concentration of M4 from 5 to 20 wt.% did not significantly lower the T_g . Figure 2F shows smooth surface morphology of the film containing 5 wt.% of M4. An increase of the concentration of M4 to 20 wt.% resulted in a phase separation as demonstrated in Figure 2G.

Thus, the slow drying method had its limitation for producing uniform films from less compatible blends. Moreover, the phase separation kinetics may be quite different compared to the dynamic creping operation. On the Yankee dryer, the adhesive coating sets up in less than one second. Therefore, a different method was sought for casting films.

Films spin-coated on mica

Spin coating was found to be more appropriate and representative of the actual process on the Yankee dryer. Freshly cleaved mica provides an atomically flat and non-contaminated surface. By having a flat surface, the effect of the substrate roughness could be decoupled from the effect of the additives. This method worked well for making very thin films (5–15 μm) that were cast within 30 s and dried at 150°C. The very small thickness allowed the film to dry quickly. After drying, the coated mica sheets were cooled in liquid nitrogen. The disadvantage of mica, however, is that Yankee dryers have a cast iron surface. Properties of the metal surface are likely to have a different effect on the adhesive films compared with mica.

The surface uniformity of these films was first studied using the SEM technique. Figure 3 demonstrates topographical images of the PAE films without additives and of the films containing 5 or 20 wt.% of release oil or modifiers. The surface of the unmodified PAE film appears to be very smooth without any significant topography. As previously observed with the cross-sections of the cryogenically fractured films, the release oil and modifiers M1 and M2 formed domains on the surface of the films. The release oil domains appeared as regularly shaped craters, while the domains created by the modifiers M1 and M2 had less regular shapes. This irregularity was especially pronounced at a 20% add-on level. Interestingly, the size of the oil craters did not seem to change with the increase of the add-on level, while for the surfactant domains, both M1 and M2, became larger with the amount of the additive in the film. The size of the release oil droplets may be governed by the emulsifying surfactants, which makes the size less dependent on the concentration.

There was no effect observed with the modifier M3 on the topography of the PAE film. The modifier M3 was miscible with the PAE polymer as

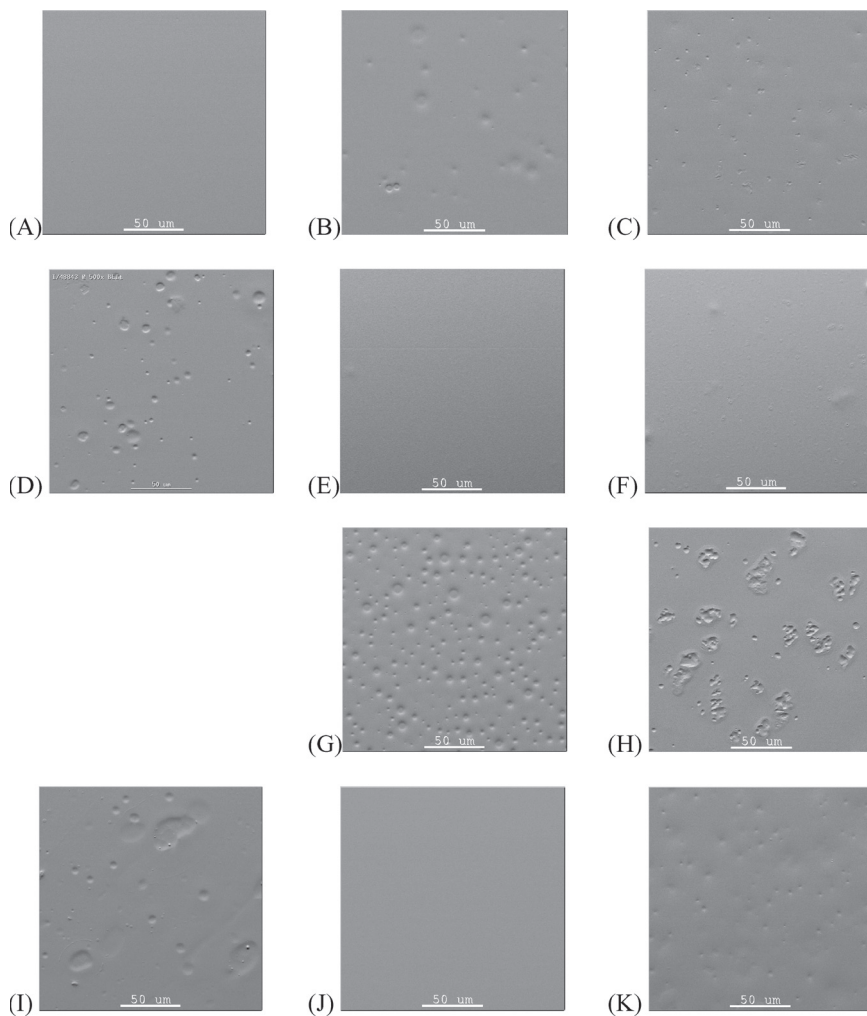


Figure 3 SEM (BEIt) images of the surface of the PAE adhesive films prepared by spin coating on mica: (A) no additives, (B) 5% RO, (C) 5% M1, (D) 5% M2, (E) 5% M3, (F) 5% M4, (G) 20% RO, (H) 20% M1, (I) 20% M2, (J) 20% M3 and (K) 20% M4. All the images were obtained at 500 \times magnification.

indicated by the Tg data. The phosphate modifier M4 appeared to create some non-uniformity on the film surface at both 5% and to a larger extent at 20% concentration. This is consistent with the Tg measurements discussed above confirming that the phosphate salt can be well dispersed in the PAE matrix, but it does not interact with the PAE polymer as intimately as the humectant.

The uniformity of the PAE films on mica was further investigated using the AFM imaging technique. Figure 4 shows a series of 3-D height images for films that were formed from PAE blended with release oil and also with different modifiers at a 20% add-on level. The roughness of the films was estimated by calculating the root mean square (RMS) values. Table 4 summarizes the roughness data.

The AFM images were consistent with the images obtained by SEM on the same samples. Figure 4A shows the image of the PAE film alone, which was very smooth, having an RMS value equal to only 0.5 nm. Images B-F in Figure 4 demonstrate the effect of release oil and modifiers on the uniformity of the PAE film. These images clearly show that uniformity of these adhesive films can be strongly affected by a release or modifying agent. The less compatible release oil (RO) and modifiers, M1 and M2, formed large domains within the film producing a very non-uniform surface with high RMS values. The surface roughness of the film modified with 20 wt.% release oil was 150–250 nm. The RMS roughness caused by surfactants, M1 and M3, was 50–80 nm. In contrast, the water-soluble, humectant-type, agent M3 had

Table 4 The effect of release oil and modifiers on the surface roughness of the PAE adhesive films cast on mica. The average RMS value and standard deviations were calculated from the values of 3–5 different locations on the same sample.

Additive	RMS (nm)	
	Average	Standard Deviation
None	0.5	0.1
5% RO	92	58
5% M1	77	5
20% RO	227	54
20% M1	67	8
20% M2	60	7
20% M3	0.8	0.1
20% M4	66	11

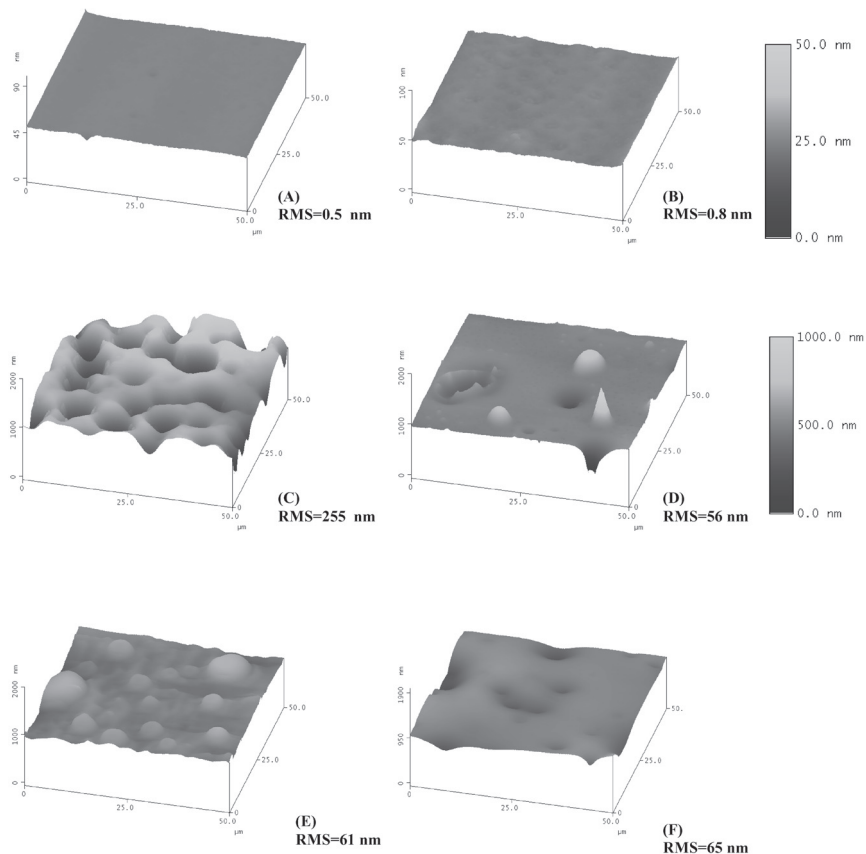
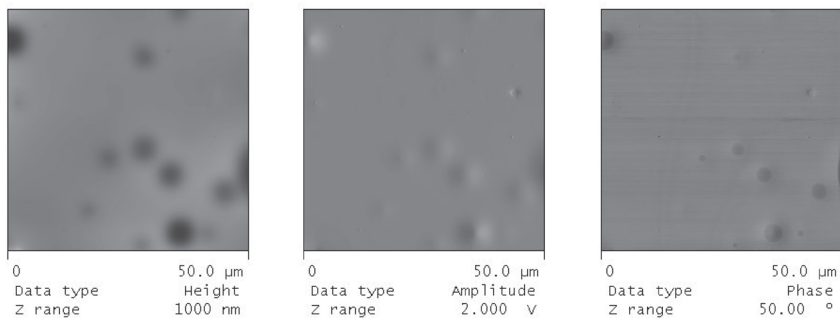


Figure 4 AFM height images (3D-projection, 30°, 30° pitch) of the PAE adhesive films coated on mica: (A) no additives; (B) 20% M3; (C) 20% RO; (D) 20% M1; (E) 20% M2 and (F) 20% M4. The imaged area is 50 $\mu\text{m} \times 50 \mu\text{m}$. The height scale for images A and B is 0–50 nm and for images C–F 0–1000 nm.

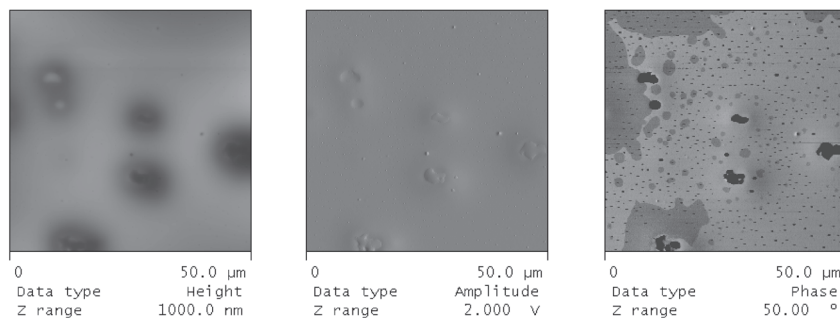
very little effect on the surface topography, resulting in an RMS value of 0.8 nm. The films modified with the phosphate M4, which is water-soluble but not as compatible with the PAE polymer as the humectant M3, resulted in a large RMS of 50–70 nm.

The nature of the domains was further investigated by using combined information from the height, amplitude and phase images obtained by the TappingMode AFM. Figure 5 shows the AFM images for the adhesive films

(A)



(B)



(C)

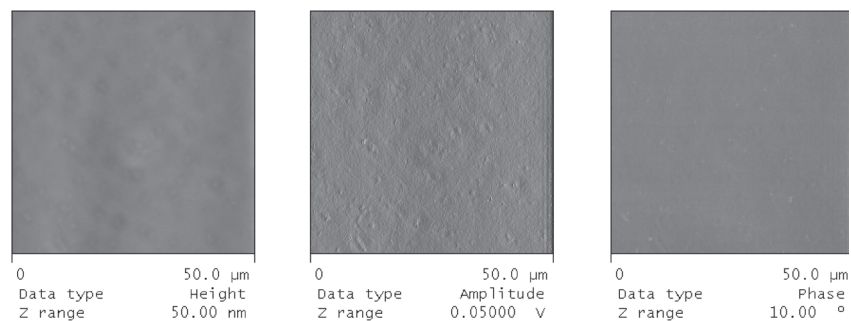


Figure 5 AFM height, amplitude and phase images of the PAE adhesive films on mica containing 5 wt.% of additives: (A) RO; (B) M1 and (C) M3.

modified with release oil (image A), the surfactant, M1 (image B) and the humectant M3 (image C). The height and amplitude images clearly show the surface topography of the film. The phase image, which is affected by both topography and by the elastic modulus of the surface, exhibits round domains in Figure 5A with phase damping properties that are very different from the rest of the film. This indicates that the nature of the material inside of the domains is very different from the PAE matrix. Most likely, the crater-shaped domains represent collapsed droplets of release oil. It does not appear from the phase image that there is any mixing of the oil with the PAE polymer.

In Figure 5B, the domains identified from the height and amplitude images as irregularly shaped depressions appear as solid-colored features in the phase image. This indicates that the domains are composed of a material different from the general polymer matrix. Most likely the domains are composed of the modifier M1. In addition to these topographical features, the phase image demonstrated that the flat areas of the film surface are non-uniform with regard to elastic properties. This suggests that the modifier M1 is partially miscible in the PAE matrix.

Figure 5C demonstrates that the PAE film modified with the humectant, M3, is not only topographically flat, but also uniform with regard to the elastic properties of the surface. This confirms that the humectant M3 intimately interacts with the PAE polymer forming a single phase, which is also consistent with the SEM and T_g data.

Films spin-coated on cast iron

The next method we pursued was spin coating on a cast iron surface both at room temperature and on the hot surface. Special phenolic resin disks with embedded cast iron coupons were manufactured for these studies (see Experimental). The cast iron surface was mirror-polished in order to reduce the effect of the surface roughness. The surface roughness (RMS) of the polished cast iron was determined from the AFM images to be 100–200 nm.

Single layer coatings

Preparing films on the cast iron surface revealed many more complications as compared to the mica sheets. Initially, the films were spin coated on the cast iron surface at room temperature similar to the method used for the films coated on mica. The SEM images of the PAE films exhibited the formation of round blister-like domains of 3–5 μm in size (Figure 6A–B). The EDS spectra taken on the general matrix (Figure 6C) and inside of the blisters (Figure 6D) showed that the amount of chlorine in the blister was much greater than

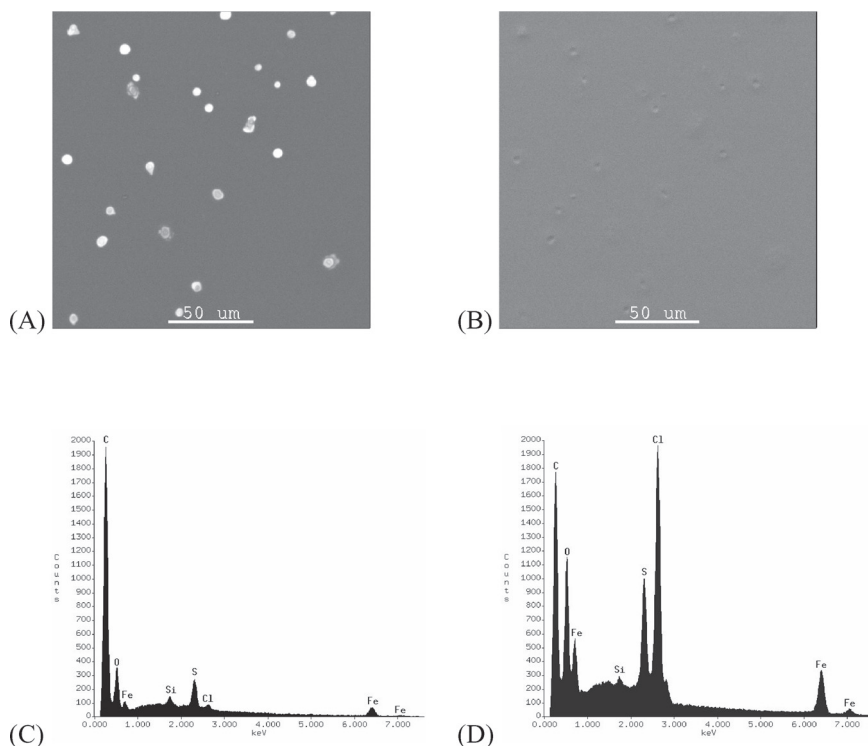


Figure 6 SEM images of the PAE adhesive films prepared by spin coating on cast iron at RT and drying at 150°C: (A) BEIac image, 500× magnification, (B) BEIt image, 500× magnification, (C) EDS spectrum inside of general matrix, (D) EDS spectrum inside of a blister.

within the matrix. Most of the chlorine is present in PAE in the form of chloride ions formed upon reaction with epichlorohydrin. The formation of spots with an increased concentration of chloride is difficult to explain except that the interactions that occurred between the chloride ions and the cast iron surface under these specific conditions promoted localized precipitation of the chloride salt. If this actually occurred on the Yankee dryer, it would mean a higher chance of localized corrosion in the areas with increased chloride concentration. Although these findings are interesting, the method of spin coating at room temperature was not a close simulation of the actual process on the Yankee dryer and, thus, the results might not be as relevant to those from an improved method that will be discussed below.

We attempted to prepare films on the same cast iron support, but at high temperature. Preheating the cast iron disks to 150°C was sufficient to maintain the coated surface temperature above 90°C for the duration of a spin cycle. The adhesive blends were also preheated to 50°C to reduce the temperature shock during the spin coating process. In the actual creping operation, water used for dilution of the adhesive is normally preheated to approx. 50°C as well. Compared with the other methods employed in these studies, by keeping the temperature of the cast iron surface high, we were able to create the film forming conditions that most closely resembled actual commercial practice. After the final drying stage, the coated disks were cooled under liquid nitrogen.

This method produced films that did not have small blisters, but instead the films contained round craters having diameters of 20–50 μm (Figure 7A). The EDS spectra (Figure 7C and 7E) indicated that the craters did not have an increased concentration of chlorine compared to the rest of the film. Instead, the amount of iron and silicon was increased indicating the film in the crater was very thin compared with the rest of the PAE matrix. The craters likely resulted from the formation of bubbles at higher temperatures and/or insufficient wettability of the cast iron surface with the PAE aqueous solution. The important outcome of this SEM study was that, under more relevant conditions, no areas with increased chloride concentration were found.

Furthermore, films of the PAE blends with various additives were made on the cast iron disks preheated to 150°C. Interestingly, at 5% release oil, the films contained only a few craters (Figure 7B) and, visually, were very smooth. Both the PAE matrix (Figure 7D) and the craters (Figure 7F) exhibited similar chemistries except inside of the craters the cast iron elements gave higher signals due to a thinner film in that area. At 20 wt.% RO, the film uniformity worsened due to phase separation. This suggested a benefit of having a small amount of a hydrophobic additive emulsified in the PAE adhesive for even coverage of a polished cast iron surface. Typical add-ons of release oil during the creping operation can reach 50–400 wt.% of the adhesive solid content. Lower levels of release are used for highly creped, soft, consumer grades where high adhesion levels are required. It might be beneficial for forming an even coating, if the level of release oil in the adhesive blend is kept low during start-ups of the Yankee dryer after grinding or cleaning. Once initial coverage is achieved, the concentration of release oil could be increased to a level necessary for control of the sheet adhesion.

With all other modifiers, large craters complicated the analysis of non-uniformities in the films and it was challenging to decouple the non-uniformity features due to poor coverage, bubbles or phase separation. Therefore, these films will not be discussed.

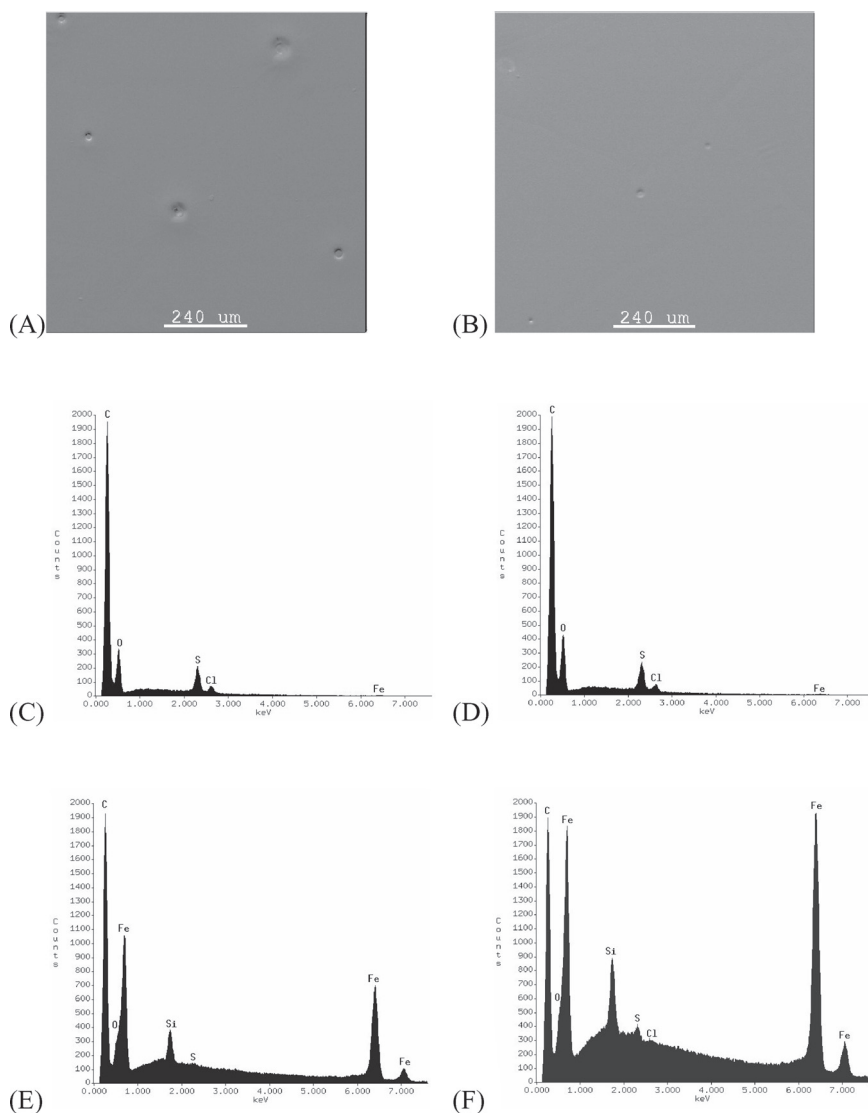


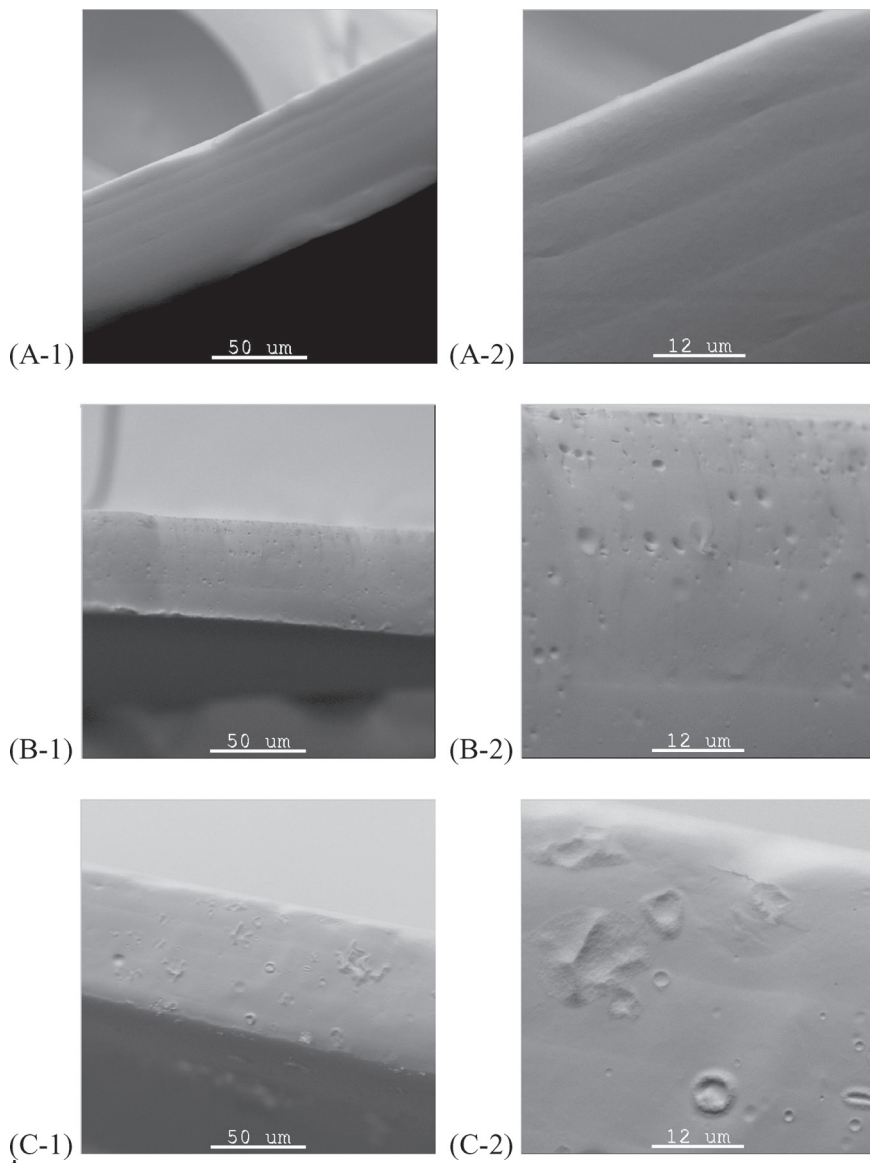
Figure 7 SEM (BEIt) images and EDS spectra of the PAE adhesive films prepared by spin coating on cast iron at 90–150°C. (A) no additives, image at 100× magnification, (B) 5% RO, image at 100× magnification, (C) EDS spectrum inside of general matrix in image A, (D) EDS spectrum inside of general matrix in image B, (E) EDS spectrum inside of a crater in image A, (F) EDS spectrum inside of a crater in image B.

Multilayer coatings

Lastly, multilayer films were also prepared by spin coating the cast iron disks five times using the same procedure described above. This procedure simulated the build-up of the coating on the Yankee dryer through continuous application of the adhesive. Prolonged drying and heating resulted in darkening of the films that also appeared harder and more brittle compared with the single-layer films, although some modifiers helped to reduce the detrimental effect of heat. On the Yankee dryer, the coating does tend to become harder and more brittle over time, which often results in excessive wear of the doctor blade and the cylinder surface from blade chatter. Release oil and modifiers are often used to stabilize the coating on the Yankee and lubricate the doctor blade [4, 5, 9].

The coverage of the unmodified adhesive films appeared uneven. The unevenness of the coverage continued to accumulate with each layer. These films also appeared hard and brittle. The films modified with 5 wt.% RO were opaque, but the coverage was very uniform and the film did not crack and appeared strongly adhered to the metal surface. At 20 wt.% RO, the films were less uniform and easily peeled off the cast iron surface after freezing in liquid nitrogen. The films modified with the surfactants, M1 and M2, were very uneven, very hard, and brittle. The films had such poor adhesion to the cast iron surface, especially at a 20 wt.% dose, that after freezing in liquid nitrogen, they simply cracked and popped off the surface. This suggested that surfactants alone at high doses may be detrimental for stability of the PAE coating on the bare cast iron surface and should not be used at start-up of the Yankee dryer. The humectant, M3, appeared to reduce the film brittleness and improve adhesion to the metal surface at both 5 and 20 wt.% doses, although the film still appeared to be uneven, similar to the unmodified film.

The greatest positive effect on the film adhesion to the cast iron surface was observed with 20 wt% inorganic phosphate, M4. Although the film turned brown, it did not crack after freezing in liquid nitrogen. Moreover, it was very difficult to scratch the film off the cast iron surface. Inorganic phosphate is known to improve runnability of a tissue machine [20]. This is believed to be due to a more even coating that is formed when inorganic phosphate is present. The results described above suggested that adhesion between the coating and the Yankee dryer improves in the presence of inorganic phosphate, which prevents the old coating layer from being easily removed. In this sense the inorganic phosphate may be thought of as an adhesion promoter between the PAE resin and the cast iron surface. Whether the improved adhesion is due to an inorganic skeleton [21] that helps hold the organic coating in place, or to a



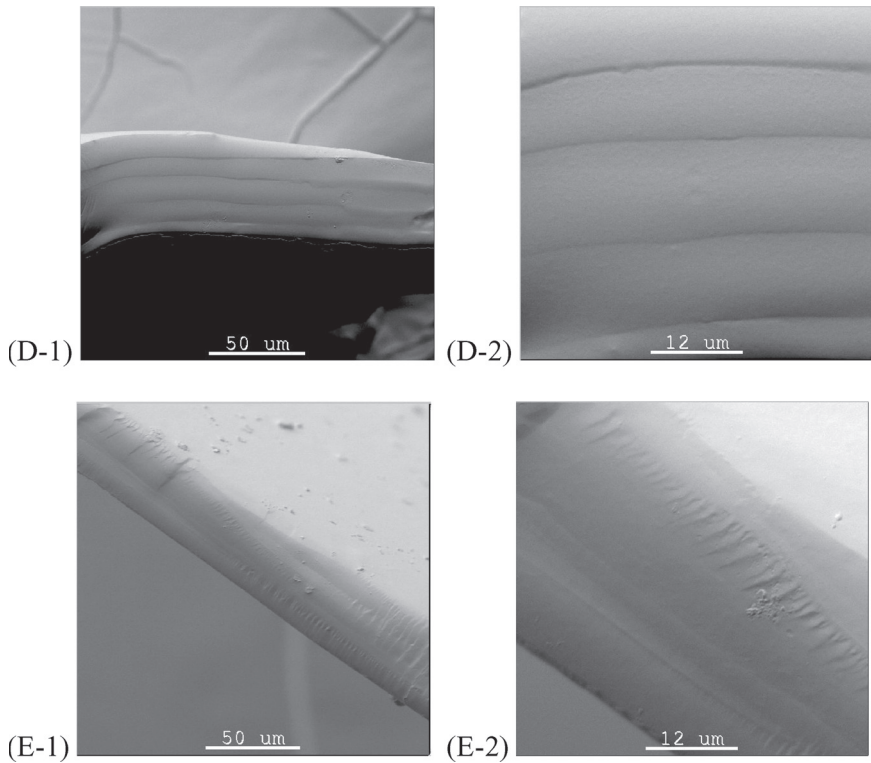


Figure 8 SEM (BEIt) images of the cross-sections of the PAE adhesive films prepared by spin coating five times on cast iron at 90–150°C: (A) no additives, (B) 5% RO, (C) 5% M1, (D) 5% M3 and (E) 5% M4. The upper layer corresponds to the airside of the film; the lower layer corresponds to the cast iron side. Images in the left column (A-1, B-1, etc.) were taken at 500 \times magnification and images in the right column (A-2, B-2, etc.) were taken at 2000 \times magnification.

specific reaction between the phosphate and the cast iron [22] remains to be proven.

The multilayer films were fractured after freezing in liquid nitrogen and SEM images were taken of the film cross-sections (Figure 8). The image of the unmodified PAE film (Figure 8A) shows that the cross-section consisted of five layers with a thickness of 10–15 μm per layer. Each layer of the film appeared to be very uniform. The addition of 5 wt.% RO resulted in the formation of round domains with a diameter of less than 2 μm within the body of the film (Figure 8B). The domains are likely to be emulsified droplets of oil. There is an indication that some droplets are aligned along the solid-solid interface. This is very different from similar films obtained by the slow drying method or by spin coating on mica where the domain distribution was random.

This domain alignment along the layer interface was even more pronounced in the films containing 20 wt.% RO (Figure 9A). In these films the droplets were significantly larger in size, up to 10–30 μm in diameter. The larger droplets appeared flattened by the adjacent upper layer of the film. The concentration of the droplets in each layer seemed to be higher near the bottom of the layer. The image of the very bottom layer (Figure 9B) that was attached to the cast iron surface had an oil droplet distribution that was very similar to the distribution observed on the surface of the film on mica, although the diameter of the droplets appeared to be more than doubled. The image of the top layer on the airside (Figure 9C) appeared to have almost no topography, which confirmed that the oil droplets favored the lower side of the layer.

This phenomenon has not previously been reported in the literature. As discussed above, the common industry belief is that oil on the Yankee dryer diffuses to the air surface driven by the heat and its low density. There are a number of possible explanations for the results reported here, including convection, driven by the temperature gradient, surface energy differences between the air and solid phases or wicking effects within the polymer matrix. The correct mechanism is currently under investigation.

The image in Figure 9B shows that the contact area between the adhesive and the cast iron surface was dramatically reduced due to the release oil, which explains why it was so much easier to remove the film containing the release oil from the substrate compared to the non-modified PAE film. The practical aspect of this data is that, if the oil tends to move towards the cast iron surface rather than to float to the outside layer, it should reduce the adhesion between the PAE layer and the Yankee dryer, especially at higher concentrations of oil that are typically 50–400% of the adhesive polymer. These data may explain the mechanism of stripping the coating off the Yankee dryer at high add-on rates of release oil.

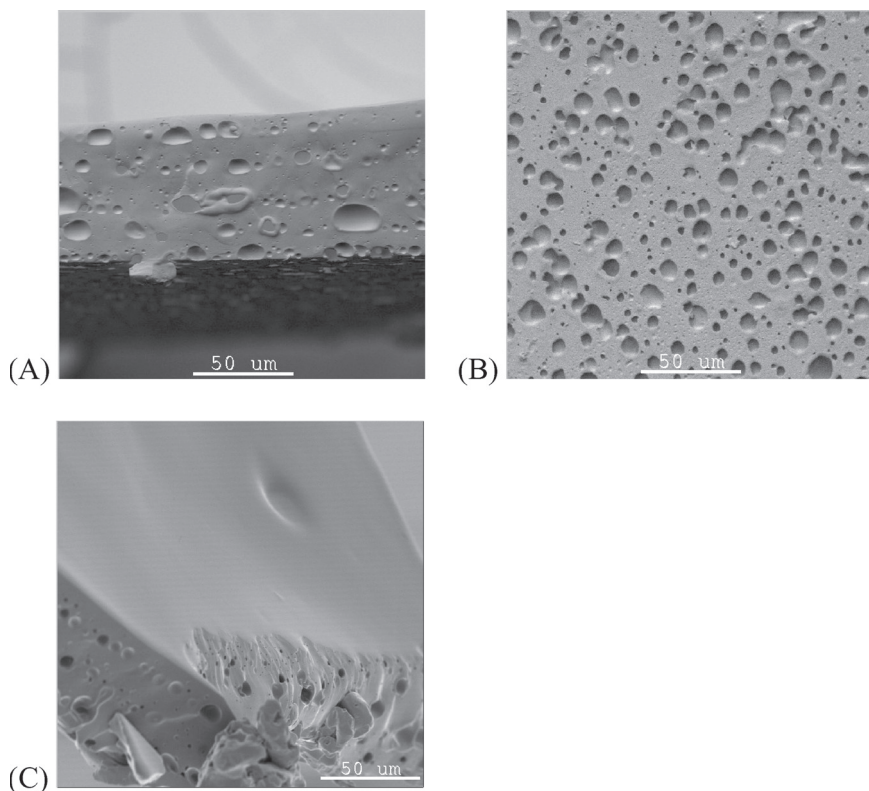


Figure 9 SEM images of the PAE adhesive film containing 20% RO. The film was prepared by spin coating five times on cast iron at 90–150°C. (A) BEIt image of the cross-section of the fractured film; (B) BEIt image of the underside (cast iron side) and (C) SEI image of the top (airside) with the film edge showing on the bottom. All images were taken at 500× magnification.

The cross-sections of the films containing 5% of the modifiers M1, M3 and M4 were consistent with the cross-section images of the analogous films made by slow drying and the surface images of the films on mica. The surfactant M1 exhibited non-uniform cross-sections with irregularly shaped domains (Figure 8C). The more compatible humectant M3 (Figure 8D) had no significant effect on the uniformity of the films, while the phosphate M4 (Figure 8E) created waviness in the film cross-section.

CONCLUSIONS

The structure of PAE adhesive films and the effect of release oil and modifiers were studied using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Film casting techniques were developed for studying the Yankee adhesives, including slow drying in a mold or spin coating on either mica or a hot cast iron surface. In general, the results obtained by using these techniques were consistent with each other. However, it was learned that variations in the film forming conditions could significantly alter the structure of the films.

Both SEM and AFM methods were found to be useful and complementary in providing information on topographical and morphological uniformity of the PAE-based Yankee coating films. The uniformity of the SEM images was consistent with that of the corresponding AFM images obtained for the same samples. The SEM technique provided visualization of both the surface and the cross-sections with a scan size up to 1 mm, compared with the AFM technique that was limited to a scan size of 0.1 mm and to a Z-height range of 4 μm . However, due to a limit on lateral resolution, SEM, unlike AFM, did not provide a means for quantification of the surface roughness. Moreover, the advantage of AFM was that it is a non-destructive technique that could operate under ambient conditions, while with the SEM technique various issues had to be overcome such as sample preparation, sample stability at high temperature and high vacuum, surface charging during imaging and other imaging artifacts. Use of an SEM capable of low vacuum operation would minimize many of the operational problems encountered in this study. The disadvantage of the AFM was that it is a slow acquisition technique and, because of the direct contact nature of the measurement, was challenging to use with some Yankee adhesive films.

The SEM and AFM images of the PAE films allowed us to demonstrate the dramatic effect that modifiers had on the adhesive film uniformity, both on the surface and in the bulk. A blend of a PAE adhesive with traditional release oil or surfactants resulted in non-uniform films, while a blend of the same adhesive with a proprietary humectant-type modifier produced a smooth film without any morphological features. The effect the humectant had on the reduction of the film glass transition temperature indicated an intimate interaction between the humectant and the PAE polymer. The more uniform film is expected to produce more uniform creping and consistent development of final tissue sheet properties. Due to these beneficial effects, we expect increased commercial use of compatible modifiers in Yankee coatings as opposed to release oils.

The SEM visualization of the PAE films containing release oil also

revealed that the oil droplets tended to migrate towards the liquid-solid interface rather than towards the air-liquid interface as has been conventionally believed. This has important implications for understanding Yankee coating structure. However, further studies are needed in order to establish the direct relevance of these findings to the actual Yankee dryer operation.

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Transcription of Discussion

DEVELOPMENT OF NEW METHODS FOR CHARACTERIZING UNIFORMITY OF YANKEE COATINGS

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Gary Baum PaperFuture Technologies

My question is why would we want to dry a Yankee coating? What kind of information do we really get from your work that is relative to the actual Yankee coating on a paper machine, since in that case the coating is not dry when it is covered by paper? The coating against the cylinder is dry, but the coating that contacts the paper is likely not.

Vladimir Grigoriev

On the Yankee, you would always have a fresh layer of the coating. In most cases, the fresh coating is largely dehydrated by the time it gets to the pressure roll. The dehydration is necessary for the coating to have the proper adhesion and durability at the pressure roll nip where the water coming from the wet sheet rewets the coating. This water may also penetrate into the older, more cured coating. The extent of the penetration will depend on the chemistry of the coating; for example, less crosslinked coatings will be easier to penetrate. One supporting example is the practical problem with stripping the coating off the Yankee when the concentration of release oil is increased to a critical point. If the old coating near the Yankee surface is not rewettable, then it should not be affected by extra release oil, but that is not the case in practice. Our observation with the model Yankee coating films showed that the oil

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droplets tend to move toward the cast iron surface which may actually explain the mechanism of how the coating stripping occurs. Another point is that at the creping blade, the coating is certainly as dry as the sheet, and for low moisture creping conditions, almost completely dry. Therefore, our model studies are consistent with what is happening on the Yankee.

Gary Baum

Well, most of the Yankee coating goes off with the paper. So, my question really is: does your work relate to the properties that are developed during the creping operation, since the coatings and the additives to the Yankee coating are essentially at the interface between the paper and the solid coating that we are making?

Vladimir Grigoriev

Some extraction studies showed that a significant amount of the coating can go off with the creped paper, but the amount is certainly determined by coating type and separating conditions. If you look at a paper towel, for example, you will not find a brown coating on the surface. In fact, if a creped sheet picks up coating chips, it would be considered a defect. So there may be some coating transfer to the sheet, but it is very minor compared to how much remains on the Yankee. Ideally, the creping blade rides just below the coating/sheet interface. As the sheet gets scraped off, some fibers and fines remain embedded in the coating and can add to the coating layer. If a cleaning blade is used, this blade removes excess coating build-up and evens out the remaining coating layer. A fresh layer of coating is then sprayed on top of this surface. Regarding the relevance of our studies to the properties of the creped paper, as I discussed in my presentation, Yankee coatings serve two purposes: adhesion and protection.

Gary Baum

So protection is what you are really talking about in your work?

Vladimir Grigoriev

The findings that I presented would be very relevant to the protection of the Yankee, but also to the quality of creping. If you do not have a stable and uniform coating, you'll have poor runnability, which will affect the quality of the creped sheet. The uniformity of the coating can be directly linked to the

uniformity of creping and hence to the uniform development of sheet properties. That is a practical fact. So, the results I presented should be relevant to both Yankee protection and the sheet properties.

Ivan Pikulik Paprican

Congratulations for addressing this difficult subject on which there is very little published. I do nevertheless have a question about the relevance of this work to actual Yankee operation. There are Yankees on which no adhesive is used develop coating anyway and that coating could, under certain conditions, be stripped. That means that a fair amount of the material of which the coating is composed comes out of the water, comes out of the pulp and probably blends with whatever you have on top of it. Would you like to comment on that?

Vladimir Grigoriev

Sure, I agree that all these synthetic chemicals are not the only components of the actual Yankee coating that forms on the Yankee dryer. Fibres, fines and various pulp extractives, for example hemicellulose, are very important components of the coating as well. However, our study is the first step to modeling the formation of Yankee coatings in the lab. We may not have been able to discover some interesting phenomena with the actual coatings due to interference from the natural materials coming from the fiber sheet. I hope our work will bring more attention and interest from researchers in this area who could continue with improving these methods. A logical continuation of our work would be to obtain an actual Yankee coating sample from a tissue machine and image it with an idea of what to look for, keeping in mind the results from our model studies. So if someone has access to a tissue machine, I would love them to get actual coating specimens and try to prove or refute our hypotheses.

Roger Gaudreault Cascades Canada Inc

Thank you very much for the interesting talk. First, did you check the molybdenum chemistry based metal because you know sometimes we are using molybdenum surface treated Yankee dryers?

Vladimir Grigoriev

No, we have not tried any other metal supports, just polished cast iron.

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Roger Gaudreault

My second question is: now that you have pointed out the non-uniformity problem and assuming that this is transferable in our mill, what could you propose to improve the non-uniformity or to improve uniformity based on your work?

Vladimir Grigoriev

It is very difficult to recommend anything specific without knowing the machine conditions and the requirements for the grades you are making. It will also depend on what adhesive you are running. However, based on the presented data, I would recommend exploring surfactant- and humectant-type modifiers as an alternative to release oils. A combination of release oil and a modifier may be, in some cases, better for optimizing all the critical properties of the Yankee coating such as adhesion, film softness, coating durability and coating uniformity. But again, this would be very machine- and grade-specific and the optimal coating package should be determined by running a machine trial.

Steven Keller SUNY-ESF/ESPRI

How significant is the non-uniformity of the surfaces? You are looking at particles and defects that are under 25 μm when the surface of the paper itself is going to have heterogeneity of the fibres that are coming in contact with the Yankee cylinder.

Vladimir Grigoriev

The non-uniformity of films made in the lab, under controlled conditions, can be viewed only as an indicator of non-uniformities that might occur under commercial conditions. The fact is that very large coating non-uniformities occur commercially, usually evidenced as “banding” or “striping”, across the cross-direction of the Yankee. The question still remains unclear regarding the relationship between the microscopic non-uniformities observed in our model coatings and the coating banding on the Yankee.

Anders Åström

I will relate my question to the last question. For the creping result you mentioned that the uniformity is important as well as the adhesion force.

Could you make some comment on the balance between these two factors? Do you need a certain adhesion force at a certain uniformity level to get a good creping result?

Vladimir Grigoriev

Yes, there has to be a balance between the adhesion and the non-uniformities due to various additives. For example, for premium tissue grades, high adhesion is necessary, but if you have too much adhesion, you will start hurting the tensile strength to the extent of destroying the sheet. In order to control adhesion, release oil or some modifiers could be used. As I demonstrated in my presentation, additives could dramatically affect uniformity of the coating. Non-uniformities may result in runnability issues, for example, coating stability, which increases the production cost due to potential breaks, off-spec product, slower machine speed and so on. So you can see that optimization is necessary to achieve adequate adhesion without making the coating too non-uniform, which could be detrimental for the machine runnability.