A new method for quantifying the blocking of coated paperboard

PAULINE SKILLINGTON, YOLANDE R. SCHOEMAN, VALESKA CLOETE, AND PATRICE C. HARTMANN

ABSTRACT: Blocking is undesired adhesion between two surfaces when subjected to pressure and temperature constraints. Blocking between two coated paperboards in contact with each other may be caused by inter-diffusion, adsorption, or electrostatic forces occurring between the respective coating surfaces. These interactions are influenced by factors such as the temperature, pressure, surface roughness, and surface energy. Blocking potentially can be reduced by adjusting these factors, or by using antiblocking additives such as talc, amorphous silica, fatty acid amides, or polymeric waxes. We developed a method of quantifying blocking using a rheometer. Coated surfaces were put in contact with each other with controlled pressure and temperature for a definite period. We then measured the work necessary to pull the two surfaces apart. This was a reproducible way to accurately quantify blocking. The method was applied to determine the effect external factors have on the blocking tendency of coated paperboards, i.e., antiblocking additive concentration, film thickness, temperature, and humidity.

Application: This test method provides a means to quantify the effect of assorted process variables on the blocking tendencies of coated paperboard.

Today's packaging industry relies on barrier coatings applied to paperboard packaging materials to protect packaged contents from contamination that could result from permeation of moisture, water, gas, or grease [1,2]. A challenge to effective coating is blocking, the undesired adhesion of two coated surfaces under the influence of temperature and pressure [3]. This effect, in the long term, reduces the integrity of a coated substrate, resulting in economic losses for the manufacturer of the packaging and the customer who uses the paperboard packing due to failure of the product to meet required performance criteria. Additives such as talc, amorphous silica, fatty acid amides, and polymeric waxes can minimize the effect of blocking [4]. These additives reduce the forces of adhesion between the two surfaces that are in contact with each other.

The most commonly used test method for the determination of blocking in coated paperboard is ASTM Standard D918-99 "Test method for blocking resistance of paper and paperboard." This is, however, a qualitative method, where the samples are stored at a specific temperature (38°C–67°C) and humidity for a fixed period. A force of 3.4 kPa is applied to samples over the test period. The samples are then subjectively evaluated on a three-point scale, where *no blocking* indicates no form of adhesion, *slight blocking* indicates only slight adhesion, and *considerable blocking* indicates complete adhesion. Standard test methods similar to this one include TAPPI T 521 "Blocking resistance of gummed flat papers" and The British Ministry of Defense Standard 81-93 "Paper, wrapping grease resisting."

Ottone and Maxwell [5] describe a quantitative method for determination of blocking that uses a heat sealer set at 65°C and 1206 kPa [175 psig]. The method uses dwell time to determine the degree of blocking, where a shorter dwell time indicates a coating with a high blocking tendency and vice versa. This method makes determination of the blocking force more objective and accurate, although the degree of blocking is quantitatively determined indirectly.

A patented method for quantitative determination of tack or blocking of areas less than 20 mm^2 involves measuring the applied current on an electromagnet that controls the measuring probe, at the moment where the probe is separated from the coated sample surface [6].

The method proposed in this paper uses a multifunctional rheometer. Its use for the blocking test is one of many different analyses possible with such an instrument. This new method provides a direct measurement of the work required to separate adjacent films or coated paperboards.

MECHANISMS OF ADHESION DURING BLOCKING

Figure 1 shows the three mechanisms of adhesion [7-10], which include the following:

1.) *Interdiffusion* – The polymer chains present at the surface of the adherent will diffuse across the interface, separating the two materials, and become entangled. Thus, the two materials will bond together. This is also known as auto-adhesion.

2.) *Adsorption* – The adhesive polymer chains are brought into contact with the substrate to such an extent that secondary van der Waals forces develop between the two surfaces, and bond the two surfaces together. Other forces that may contribute to this type of adhesion are acid-base interactions and hydrogen bonding.

3.) *Electrostatic interactions* – The difference in electronegativity between the two adhering surfaces results in the movement of electrons (towards the more electronegative surface) across the interface between the two materials. Thus,

a positive charge and a negative charge are created on either side of the interface, which attract each other, resulting in the two surfaces bonding together.

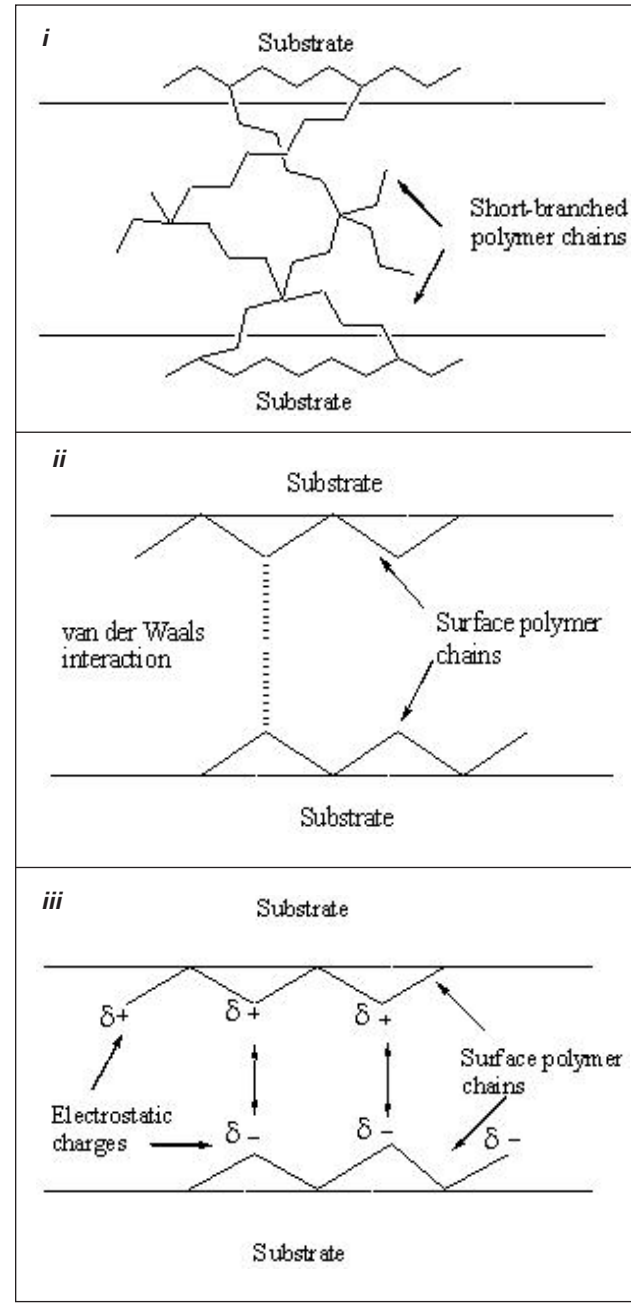
PARAMETERS INFLUENCING BLOCKING

Based on the mechanisms of blocking described previously, the following parameters influence blocking:

- **Migration and diffusion** — Migration of additives such as plasticizers or short-branched chains to the surface must be prevented because they might diffuse across the interface between two coated surfaces, causing blocking. On the other hand, antiblocking additives added to the coating formulation to prevent blocking must migrate and become immobilized at the film surface [3].
- **Temperature of production and processing** — High processing temperatures promote the viscous modulus of the polymeric coating, hence increasing its tackiness [11].
- **Pressure under which the material is used and stored** — Pressure or winding strain increases contact between layers, hence maximizing the inter-chain diffusion between the coated surfaces [9].
- **Morphological and/or chemical structure of the surface layers** — The morphology and chemical structure of the surface layers are dependent on the conditions under which the films are formed. Two important factors to consider are the structure of the film's surface layer and the effect of the matrix components on the surface layers.
- **Surface roughness** — Microscopic surface roughness prevents close contact between two surfaces, thus minimizing the molecular interactions between the two surfaces [12]. Microscopic surface roughness also might decrease the molecular interactions, resulting in decreased blocking forces [13].
- **Electrostatic and other similar forces** — Particles with opposite charges are attracted to each other. This is the manner in which the inorganic antiblocking additives bind with the organic material, but not to each other.
- **Film thickness** — Tordjeman et al. [11] proposed that adhesion between two surfaces, under the influence of temperature and pressure, is related to film thickness. Above a certain critical film thickness, the viscous modulus of the film becomes large enough to enable energy dissipation and adhesion between the two surfaces subsequently reaches an optimum level. Below the critical film thickness, the elastic modulus of the film is high, thus restricting the energy dissipation, leading to poor adhesion between surfaces.

MECHANISMS OF ACTION OF ANTIBLOCKING ADDITIVES

An antiblocking additive can be effective only if it migrates from the bulk of the coating and becomes immobilized at the coating surface. In waterborne polymer latex coatings, the migration of the additive during the drying process of a coating occurs in two directions: toward the base paperboard substrate during the aqueous phase drainage and toward the coating surface during the aqueous phase evaporation.



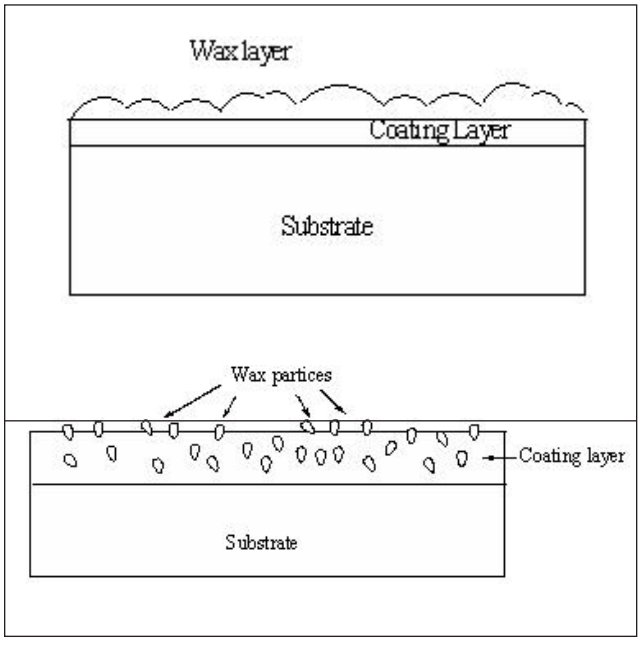
1. Mechanisms of adhesion: i) interdiffusion, ii) adsorption, and iii) electrostatic interactions.

The following six-step process describes the mechanism of additive migration [14]:

1.) The polymer latex is coated onto the substrate. All the pore spaces are full of liquid and the additive distribution is uniform.

2.) The liquid present on the coating surface starts to evaporate. In the initial stages of evaporation, the liquid level recedes slightly and remains lodged in the surface pore passage. Liquid is drawn from the base of the coating film (where evaporation does not take place) by a capillary pressure difference to feed evaporation.

3.) The additive is drawn toward the surface due to the



2. Mechanisms of wax migration: i) blooming mechanism and ii) ball bearing mechanism.

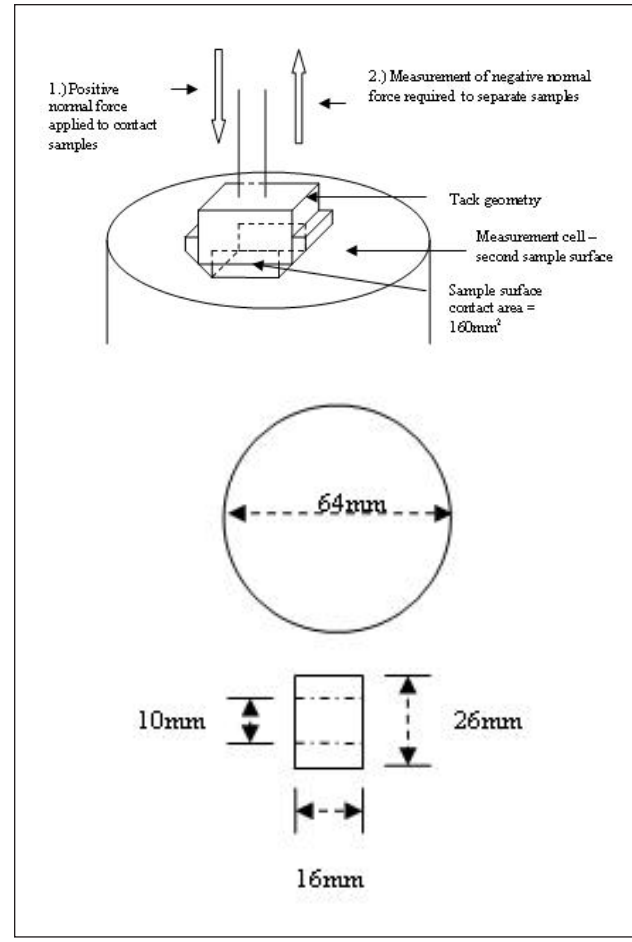
movement of liquid and concentrates at the evaporating surface. If the rate of convection toward the evaporating surface is faster than the rate of diffusion away from the surface, the additive reaches saturation and precipitates at the surface.

4.) The liquid level in the surface pore passage decreases as evaporation proceeds. The liquid is propelled into and perhaps beyond the connected pore body, after the liquid has completely wet out the pore passage.

5.) The drying rate decreases. The liquid evaporating from the pore body must diffuse through a pore body and a pore passage to reach the surface.

6.) The drying rate will drop even further as the liquid level recedes further. The evaporating liquid will have more pore bodies and pore passages to travel through before reaching the outer surface. Isolated groups of liquid-filled pores will eventually shrink and restrict the number of pathways, whereby the capillary-driven flow can transport the evaporating liquid to the outer surface. The rate of drying is highly dependent on the internal resistance to mass transfer.

The mechanism described above applies to the various inorganic antiblocking additives such as clays, talc, and pyrogenic silica. However, in the case of polymeric waxes, two specific mechanisms of additive migration have been described [15,16]. The first is the *blooming mechanism*, during which the molten wax particles float to the surface and recrystallize upon cooling. This results in formation of a thin, continuous wax-enriched surface layer. The mechanism is more compatible with the softer waxes, and the migration of the wax is increases with the growing incompatibility between the wax and the coating. The second is the *ball bearing mechanism*, by which the solid wax particles migrate to the surface individually and protrude above the coating surface, thus preventing interdiffusion and chain entanglements between the surfaces. The particle density and degree to which the wax particles protrude above the surface determines the effectiveness of this mechanism. Hard and high-melting-point waxes are best suited for this mechanism. Fatty acid amides migrate to the surface of a coating via a similar mechanism [17]. **Figure 2** illustrates the two diferent mechanisms of wax migration.

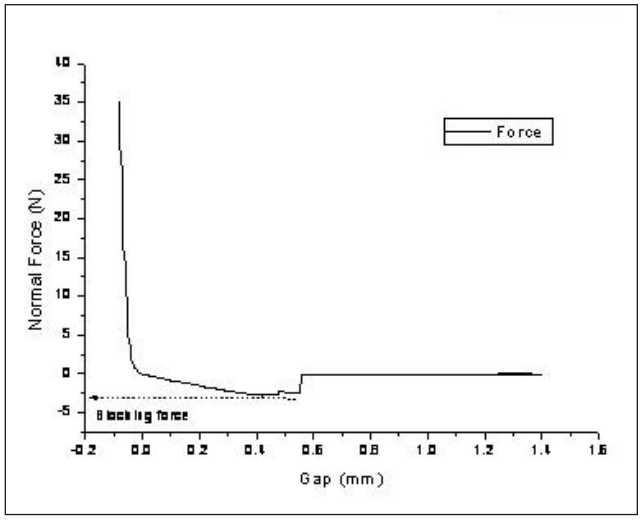


3. Schematic representation of the new quantitative blocking method.

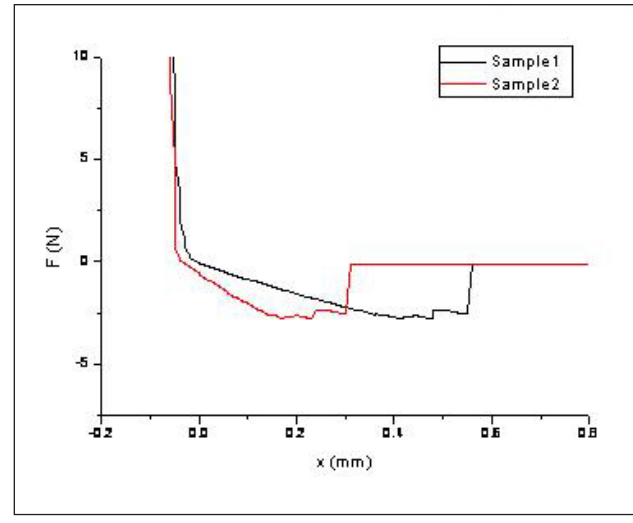
THE NEW DIRECT QUANTITATIVE MEASUREMENT METHOD

The new method is based on the measurement of the work required to separate adjacent surfaces after being exposed to a preset temperature and pressure. First, the adjacent sample surfaces are brought into contact with each under a positive force for a preset time at a specific temperature and pressure, the total contact area being 160 mm². Thereafter, the two surfaces are pulled apart at a constant rate. The blocking force is recorded as the lowest negative force measured while both surfaces are pulled apart from each other. **Figure 3** shows the new quantitative blocking method test setup.

Figure 4 shows a typical blocking force curve that is gen-

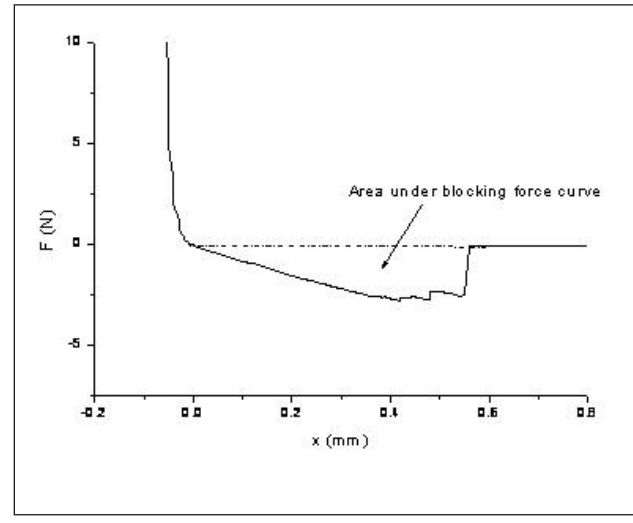


4. Typical blocking force curve (as seen on rheometer).



5. Comparison of the two samples having the same maximum blocking force.

erated during the test. However, the use of the blocking force does not always give a true indication of the blocking tendency of the sample. **Figure 5** shows the typical blocking force curves of two different coated samples. Although the absolute value of the maximum force needed to separate the blocking surfaces was the same, the work of adhesion differs. The work to separate the two adjacent surfaces is supplied by an external force generated by the rheometer. The degree of separation between the adjacent surfaces also is measured by rheometer and is therefore a similar approach to the mechanical probe test, which can be used to quantify the work of adhesion. The results of the blocking test yield a force-displacement curve. The area under the curve for negative values of F would be a measure of the work done to separate the two surfaces from each other. The work done ($\int_0^\infty F_x dx$) by the external source divided by the contact area (A) between the two adjacent surfaces is then defined as the work of adhesion (W_{adh}) [18]. **Figure 6** shows the force-displacement curve where the area under the curve is determined.



6. Force displacement curve used to calculate the work of adhesion.

$$W_{adh} = \frac{\int_0^\infty F_x dx}{A} \quad (1)$$

where W_{adh} is the work of adhesion (J/m²), F_x is the attractive normal force measured during the elemental displacement dx (N), and A is the surface contact area between the two surfaces (m²).

EXPERIMENTAL

Sample preparation

To prepare the latex–wax blends, we added an anionic paraffin/polyethylene wax emulsion with a melting point of 55°C to a styrene-based acrylic latex with a glass transition temperature of 5°C, in a concentration range of 0%–10% (in 2.5% increments), based on the solid content of both the coatings and the wax.

To prepare the coated paperboard samples, we applied the latex–wax blends to the surface of a surface sized cellulosic substrate with a wet film thickness of 12 µm (as per supplier specifications [19] using a draw-down coating machine). The coated substrate was placed in an oven to cure at 110°C for 1 min. The cured samples were then placed in a humidity cabinet at 23°C, 50% relative humidity (RH), for 24 h before analysis.

To prepare the coated paperboard samples for humidity testing, the coated samples were prepared as described above. The conditioned samples were then stored at 10%, 50%, and 90% RH for 24 h before the blocking force was determined.

Sample analysis

Blocking force and dynamic mechanical analyses

We used a rheometer, equipped with an immobilization measurement cell and maintained at 45°C by water circulation and tack geometry, to measure blocking force. Samples were cut from the coated board samples (Fig. 3). The adjacent sam-

ple surfaces were pressed against each other with a pressure of 6.25 kPa (1 N) for 10 min, at 45°C. After the initial equilibration time, the two surfaces were pressed together with a pressure of 218.75 kPa (35 N) for 30 min. Thereafter, the two surfaces were pulled apart at a speed of 0.1 mm.s-1

We also used the rheometer, equipped with a plate measurement cell and plate geometry, for the dynamic mechanical analysis. To prepare the sample coating films, we allowed water to evaporate from a sample of the latex (6 mL) in a 47 mm-diameter circular aluminium form, at 23°C. We then stored the films at 10%, 50%, and 90% RH for 24 h. The temperature was reduced from 50ºC to –20ºC at a rate of 1ºC/min, during which we recorded the storage and loss modulus by performing an oscillatory test within the linear viscoelastic range (frequency = 1 Hz, amplitude = 0.1%)

Surface roughness and energy analysis

We used a Parker print-surf tester to determine the surface roughness and a contact angle analyzer to determine the surface energy of the coated surfaces. The three-liquid harmonic method was used, making use of the values of the contact angles formed with the following liquids: water (72.8 mN/m), ethylene glycol (47.7 mN/m), and diiodomethane (50.8 mN/m). The samples were analyzed at 23ºC.

Sorption analysis

For sorption, we used an intelligent gravimetric analyzer. A film of the sample coating with a thickness of 5 mm was prepared. Analysis was performed in the vapor mode at 20ºC. The partial pressures of water used in the moisture sorption analysis were equivalent to 10% RH (2.3 P/P_0), 50% RH (11.8 P/P_0), and 90% RH (21.2 P/P_0).

RESULTS AND DISCUSSION

The method of determination of blocking was validated by quantitatively evaluating the impact of various coating and environmental parameters on the blocking tendency as related to the work of adhesion.

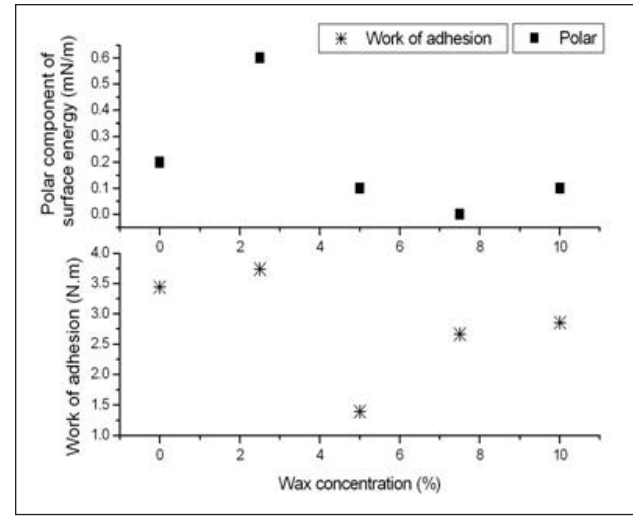
Effect of surface polarity on blocking

Figure 7 shows the effect of increased wax concentration on the work of adhesion and the polar component of the surface energy. As the wax concentration was increased, the work of adhesion and the polar component of the surface energy decreased.

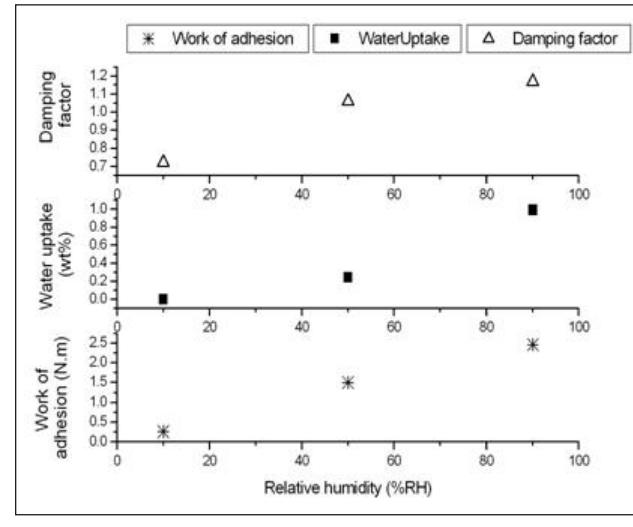
Surface energy is broken into two components, the dispersive component (γs^d) that accounts for the electrostatic interactions and the polar component (γs^p) that accounts for hydrogen bonding and polar interactions [20]:

$$\gamma s = \gamma s^{p} + \gamma s^{d} \quad (2)$$

The blocking tendency was directly related to the polarity, hence the polar component of the surface. This is consistent with the findings of Novak et al. [21], and the conclusions of Hazlitt et al. [12], who stated that blocking is due to van der Waals interactions occurring on the surface.



7. Effect of increased wax concentration on the work of adhesion and surface energy of styrene acrylic latex.



8. Relationship between work of adhesion, moisture absorption, and degree of plasticization.

We also observed that the blocking force began to increase again above 7.5% of wax. The reason for the increased blocking tendency could be related to the thickness of the wax layer on the surface of the film. The molten wax particles float to the surface of the film as it cures and recrystallizes to form a continuous wax layer, as described in the blooming mechanism. The probable reason for the increase in blocking tendency above 7.5% of wax could be that the wax film is above the critical thickness and, as a result, chain entanglements could be occurring due to the long chain lengths of the polyethylene and paraffin components of the wax [22].

Effects of humidity on blocking

Figure 8 shows the effects of increased relative humidity on the work of adhesion, damping factor, and mass uptake at

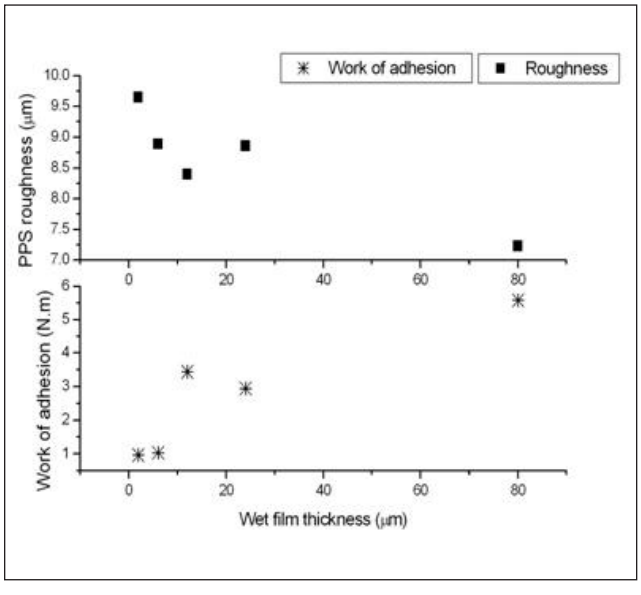
25ºC. We observed that as the relative humidity increased so the work of adhesion, damping factor, and mass uptake also increased. The damping factor is defined as the ratio between the loss modulus (G'' – viscous component) and storage modulus (G' – elastic component):

$$Tan\delta = \frac{G''}{G'} \quad (3)$$

The increase in the damping factor is indicative of an increase in the loss modulus (G'') of the films relative to the storage modulus (G') as a result of plasticization due to increased moisture absorption. This was consistent with reports in literature, which stated that water-induced plasticization promotes the rubbery modulus [22-24]. This is the main contributing factor to the increased blocking tendency [25,26].

Effect of film thickness on blocking

Figure 9 shows the effects of film thickness on the work of adhesion and surface roughness. As the film thickness increased, so the surface roughness decreased and the work of adhesion increased. This is in direct agreement with the findings of Jovanovic et al. [27]. We also noted that the increased film thickness resulted in a smoother surface. The increased blocking tendency could result from an increasing contact area between the two surfaces, facilitating inter-diffusion and chain entanglements. It also might be explained by a theory proposed by Tordjeman et al. [11], according to which above a critical film thickness the viscous modulus is high, resulting in chain entanglements between the two surfaces. Blocking between the two surfaces is at an optimum level. Below a critical film thickness, the elastic modulus is large and limited chain entanglements occur. Therefore, the blocking between the two surfaces is minimal.



9. Relationship between work of adhesion and surface roughness with increasing film thickness.

CONCLUSIONS

We developed a new quantitative method for measuring the work of adhesion due to blocking between adjacent films. The benefit of this method is that the analysis can be performed on a commercially available rheometer, which is multifunctional.

We also validated the method and proved that the influences of variables such as wax concentration, relative humidity variations, and film thickness on the degree of blocking were consistent with trends previously reported in the literature. **TJ**

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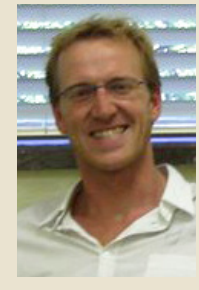
ABOUT THE AUTHORS

Skillington



Hartmann

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The tendency of a barrier coating to show blocking may determine the success or failure of production or trial runs. The ability to quantify this tendency on a laboratory scale enables action to be taken to minimize or eliminate the blocking tendency.

In this study, we successfully validated the proposed test method by which the effect of certain variables on the blocking tendency were proven to be consistent with trends previously reported in literature. Although reproducibility was initially a major concern, this was quickly remedied by conditioning the samples to a constant temperature and relative humidity.

From this study we discovered that the phenomenon of blocking is very sensitive and small changes in parameters, such as temperature, relative humidity, etc., can mean the difference between no blocking and severe blocking. We also determined that the effect of blocking can be eliminated during product development before proceeding to trial, thereby minimizing the possibility of blocking-induced problems on production and converting lines.

The test method will be used on an ongoing basis to determine whether the blocking tendencies observed in the laboratory correspond to online manufacture.

Skillington and Hartmann are with Mondi Packaging South Africa Research Centre, Department of Forest and Wood Science, University of Stellenbosch, Matieland, South Africa; Schoeman is with Mondi Packaging South Africa, Felixton Mill; and Cloete is with Mondi Packaging South Africa, Springs Mill. Email Skillington at pauline.skillington@mondigroup.co.za.