

How items such as dust, oligomers & slip agents can affect the polymer film surface quality and be potential problems in high-tech roll-to-roll vacuum deposition applications.

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ABSTRACT

There is often a contradiction in the requirements asked of polymer films. Often they are required to be perfectly flat & smooth which could be achieved but to the detriment of ease of winding. It is no use producing a very smooth & flat surface if the film cannot be wound up without blocking &/or surface damage occurring. Methods to reduce this problem are to add fillers that provide bumps on the surface to encourage air to be entrapped & reduce the contact area or alternatively to coat one surface with slip agents. The slip-agents by their nature often can be transferred from one surface to another or even migrate through the polymer web thickness. These can be a source of poor adhesion to subsequent coatings.

Oligomers are a by-product of the polymerisation process. Oligomers are a low molecular weight residue that will be present on the surface & through the bulk. It is possible to clean the surface but over time these oligomers can diffuse from the bulk back to the surface.

This paper will elaborate on these issues & what might be done to manage the films to make a useable substrate.

INTRODUCTION

There are many reasons for interest in the surface of polymer webs. The traditional users for metallization continue to have problems with quality and adhesion. Many of these problems can be related back to the polymer composition, residual oligomers, migration of low molecular weight organics as well as dust and debris on the surface. Newer uses for polymer webs are in the area of flexible electronics such as flexible displays of which the organic light emitting displays is a current favourite. The other area of developing interest is in nanotechnology.

These newer applications take the polymer surface requirements to a new level. Many of the requirements want a degree of perfection of the coatings that need the polymer substrate surface to be as smooth, flat and as contamination free as possible. In earlier papers I have referred to the surface contamination on the polymer and the possible cleaning techniques such as ultrasonic pulsed gas cleaning and tacky roll cleaning (1). In both of these techniques the best that can be achieved is to reduce size of the debris that remains on the surface down to 0.3 microns. Debris of this size is still as large as the thickness of the active coatings for OLEDs and is many times the line widths of the circuitry that is envisaged.

Barrier coatings, irrespective of whether they are metallized and used for food packaging or transparent barriers used in displays, all are adversely affected by pinholes in the coating that are directly attributed to the levels of surface debris present at the start of coating (2). Additional problems can arise if the coatings have poor adhesion. A lack of adhesion prevents any stresses being transferred from the coating to the substrate. If the stress cannot be transferred the coating will be prone to cracking at lower stress levels and cracks will be additional route for gases to pass through reducing the barrier performance.

Another area of ongoing concern with all polymers relates to any potential adverse affect on human health particularly where there is food contact. Thus there is interest in the chemistry of the polymer surface and the rate of migration of any chemicals to the surface. In fact there is much information on the migration of oligomers available from work done testing of polymers for food contact approval (3,4).

Thus we can see there is great interest in improved surfaces for most applications.

TERMINOLOGY

Blocking.

This is where two polymer webs once brought together cannot slip against each other and in some instances may not be easily separated. This can occur during processing and/or during storage of the film. This can be made worse by processing at elevated temperatures and/or increased pressure. Thus tightly wound warm films are much more likely to block than lower hardness ambient temperature rolls. Blocking can be controlled by the use of anti-blocking additives and/or slip agents.

The tendency to block can be measured in accordance with ASTM 1893 – 67 and ASTM 3354. The first of these tests measures blocking & the second re-blocking.

Blocking is worse for smoother film surfaces, for films with high electrostatic charge and for films with a high surface energy such as those corona treated.

Anti-blocking additives.

These are fillers that are added to the polymer that will increase the surface roughness. The effect of this is that the two surfaces are kept apart by the fillers that protrude from the surface. This in turn reduces the contact surface area and when winding in air guarantees an amount of entrained air between the polymer surfaces. The effectiveness of the filler is dependent upon the number of fillers and the size and hence height that the fillers protrude from the surface. Anti-blocking fillers do not migrate after the polymer has solidified and so only a limited amount of the filler added will be present at the surface. As they increase the surface roughness they increase the haze and reduce the specular reflectance. Typically the haze increases by 0.4-1.0% per 1000ppm of silica filler used. Thus there is a balance between the ease of handling and the optical performance. It is also common for a combination of anti-block filler and slip agent to be used in order to minimize the impact on the optical performance. Also it is common to find co-extruded films with a thin outer layer including the filler to provide the handling performance but because the bulk of the thickness does not contain filler the optical quality is kept high.

Filler types can vary in shape, size and hardness. Some examples are as follows.

Synthetic silica – high surface area, hydroxylated and microporous surface. A good match of

refractive index for PE & PP and used to make highly transparent films.

Natural silica – a different mixture of shapes and sizes and often contains impurities that the synthetic silica does not. Cheaper than synthetic silica.

Talc – Magnesium hydrosilicate, a lamella type of soft rock that has a refractive index that is also a good match to PE & PP.

Limestone – A low cost filler. Calcium carbonate and sometimes a mixture with magnesium carbonate these are used in lower quality film applications.

HDPE, paraffin and carnauba waxes are typically used in coatings to counteract blocking. The use of anti-blocking fillers can reduce the Coefficient of Friction (CoF) down to 0.3–0.4 which may still be higher than required and so slip additives may be used in conjunction with the fillers.

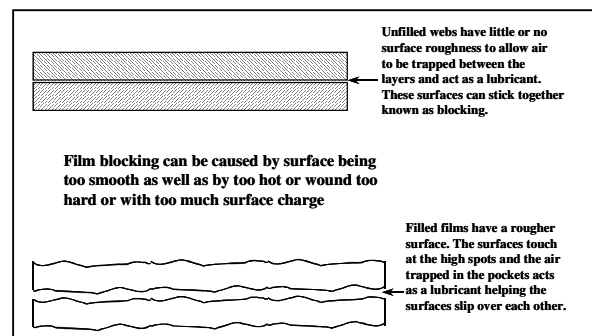


Figure 1. A schematic of the cause of blocking

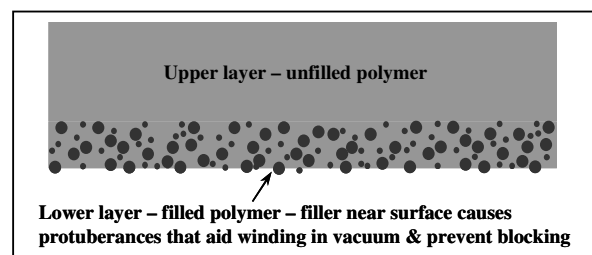


Figure 2. A schematic of a filled co-extruded polymer film that provided improved handling with a thin filled co-extruded layer with a thicker unfilled front surface that gives a smoother surface.



Figure 3a) Melinex 'S' b) Melinex '442' c) Melinex 'O'
Differential Interference Contrast (DIC) optical microscopy micrographs.

Melinex 'S' contains more fillers than '442'. The 'O' grade is the optical grade and contains minimum fillers. The 'O' grade also shows a line of damage where something has contacted the surface and caused a plucking type defect.

Slip effect.

This is the term applied to polymer films where there is the sliding of parallel polymer web surfaces over each other or over of one polymer surface over some other surface.

Coefficient of Friction (CoF)

The resistance to slip is measured as the Coefficient of Friction.

The measurement of this gives two measures, the static CoF, which is the force, required to initiate slip and the kinetic CoF, which is the force, required to keep the movement going at a pre-determined speed. The measurement of CoF of polymer films is described in ASTM D 1894 – 73

CoF of LDPE can be up as high as 0.7 but with 0.1% slip additive it can be reduced to below 0.2 where 0.16 – 0.2 CoF is regarded as acceptable for easy processing.

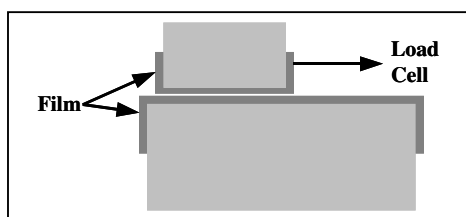


Figure 4 Method for measuring coefficient of friction.
Two layers of film are in contact with each other with an applied load and the force used to pull one film over the surface of the other is measured.

Slip agents.

These are the materials added to reduce the CoF. They are frequently added during the mixing and extrusion stage and operate by migrating through the polymer bulk to the surface. The slip agents have a designed incompatibility with the bulk polymer so that they are not bonded into the bulk but are free to migrate. The size of the molecule determines the ease of which the

slip agent will migrate through bulk polymer. The slip agents can be tuned by increasing the molecule chain length by adding or subtracting carbon atoms. Adding more atoms increases the chain length and slows down the speed of migration it also increases the compatibility with the host polymer.

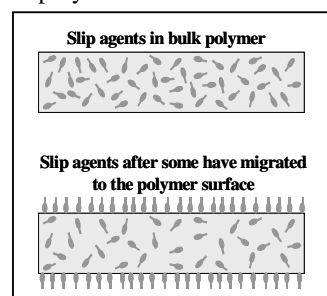


Figure 5. A schematic of the effect of slip agents.
Initially the slip agent is distributed throughout the bulk of the polymer. This is shown in the upper schematic. The lower schematic shows what happens after some time or with an increased temperature and some time. The slip agent has migrated through the polymer and a significant proportion resides on both the surfaces.

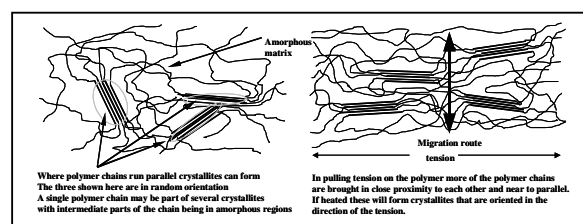


Figure 6. A schematic showing how polymer films change with orientation and how migration can be restricted with increasing crystallinity.

The speed of migration is also affected by the bulk polymer structure. Polypropylene (PP) is more crystalline than polyethylene (PE) and so the migration is slower in PP than in PE. The slip agents are solubilized into the polymer when it is molten but as the polymer cools it is precipitated out of the polymer that crystallizes and acts as a lubricant. Figure 6 shows that if there is a proportion of amorphous polymer there will be a migration route through the polymer.

Slip agents not only reduce the CoF but also are used to reduce adhesion between the mould and injection moulded polymer. The slip agents have exactly the same effect on metallisation and reduce adhesion. It is worth noting that there is no control over which surface the slip agents appear on. They will migrate to both surfaces thus if preparing a surface for vacuum coating it is no use treating one side only before putting the roll into the vacuum system. After an atmospheric treatment the side

treated will be brought back into contact with the other surface as the roll is wound up and hence will become re-contaminated. In vacuum treatment will allow the surface to be coated before it is recontaminated however the freshly deposited coating will become contaminated as the roll is wound up. Thus there may not be an adhesion problem with the vacuum coating but there may be on the next coating applied to the vacuum deposited coating.

Some slip agents are produced by the amidisation of long chain fatty acids. Examples of the most commonly used of these are Steramides, Erucamides & Oleamides.

Erucamides are longer chain, more heat stable and more oxidation resistant than Oleamides and with a lower vapour pressure create fewer volatiles during high temperature processing. The Oleamides migrate through to the surface more quickly and are sometimes referred to as 'fast blooming'. The aim is to provide sufficient slip additive so that with a suitable time for migration no more than a monolayer will have accumulated at the surface. More than a monolayer does not make any further improvements on the slip performance.

Stearamide is prepared by amidation of stearic acid (C18:0). Mpt. 98-104 °C

Oleamide is prepared by amidation of oleic acid (C18:1). Mpt. 66-76 °C

Erucamide is prepared by amidation of erucic acid (C22:1). Mpt 79-85 °C

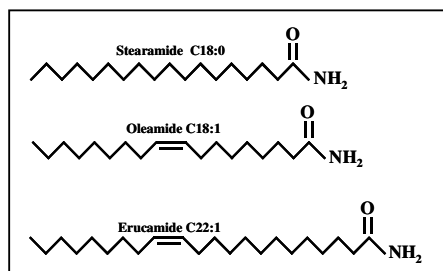


Figure 7. A schematic of the three basic slip agent structures.

Waxes can also be used as slip agents. Waxes are similar to oils except they are solid at ambient temperature and generally have a melting point in excess of 40°C. A very interesting evaluation study with microcrystalline waxes clearly demonstrated that the harder the wax, the better the slip properties.

Additives.

There are other chemicals added to the polymer melt in order to assist producing the precise film performance that is expected of modern polymer webs.

The list of additives has increased with time and now can include the following.

- Nucleation promoters
- Anti-oxidation
- Radical scavengers
- UV absorbers
- Cross-linking agents
- Gloss improvers
- Surface active agents
- Anti-static
- Anti-mist
- Slip or lubricants
- Anti-blocking fillers
- Colour (pigments or dyes) and/or whitening agents (optical brighteners)
- Voiding agents
- Viscosity modifiers
- Dispersion stabilisers
- Flame retardants
- Foaming agents

In PP the crystallisation process, which controls stiffness and clarity, is helped by the addition of a nucleation additive such as benzoate salts (sodium, aluminium, potassium) or sorbitols are used at levels of up to 0.5%.

PP is prone to oxidation and so phenolic or phosphite type anti-oxidants are added at levels between 0.01% to 0.5%.

Anti-static additives such as glycerol monoesters or ethoxylated secondary amines are used at concentrations between 0.1% and 1.0%. These additives are hydrophilic and also have limited solubility in the polymer and so they too migrate to the surface where they are most effective.

The anti-mist agents are similarly hydrophilic and may be added as an additive or applied after as a coating.

Colorants & whitening agents are too diverse to list and may or may not be stable in the polymer

Oligomers

If we consider the polymer film polyethylene terephthalate (PET), it has many inherent properties such that it does not need some of the additives that are used to enhance the performance of polypropylene (PP) or polyethylene (PE) films.

PET does have a problem with the production of residual oligomers during polymerisation and subsequent processing. Unpolymerised monomer can volatilise from the surface of the polymer film and may condense and fall back to the polymer film surface as a white powder. There

will be much more unpolymerised or incompletely polymerised monomer within the bulk of the film. As with slip agents this low molecular weight material can migrate through the amorphous regions of the PET and accumulate on the surface. Usually this will be at low levels and small enough to be invisible to the eye.

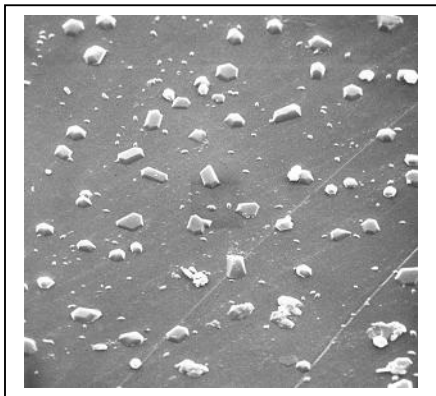


Figure 8. A micrograph of Melinex '442' that has been subjected to prolonged heating at 140°C. Scanning electron microscope Magnification 2000x Showing the growth of 'mer' (dimers, trimers..... hexamer) units into substantial crystals

Figure 8 is of a film that has been heated to encourage this migration and the oligomer has grown into the characteristic angular shapes shown in the micrograph. These short chain monomer units are not well bound into the surface and so, if not removed, form a weak boundary layer that once coated exhibits poor adhesion. The oligomers can have a variety of forms and different molecular weights, some of which have a low melting point (5-9).

It is worth noting that PET is often referred to as being amorphous or crystalline. This can be a misleading statement. Amorphous PET in reality is a mixture of approximately 60% amorphous and 40% crystalline PET. Similarly crystalline PET has approximately 60% crystalline and 40% amorphous PET. Hence both have plenty of amorphous regions such that migration can take place although it is slower with the crystalline PET where the migration path is likely to be more tortuous.

These can be present in the bulk around 1% - 3% depending on the process and conditions used. Usually there is a cost versus performance balance that has to be traded so that PET film can be obtained with extractable oligomer levels <0.5% but these are sold at premium. Approximately 90% of the extracted material is cyclic trimer, a specific PET oligomer common in all PET films.

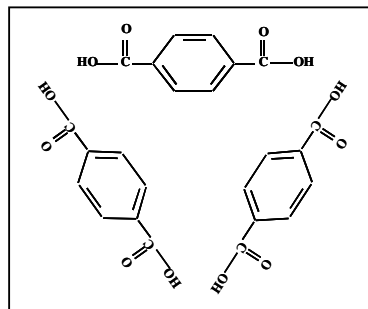


Figure 9. Cyclic tris(ethylene terephthalate) 'cyclic trimer' – oligomer, 2 dimensional representation.

Extraction refers to the method of determining the quantity of oligomer in the polymer. A simple process of washing the polymer in a suitable solvent, e.g. xylene, will remove the surface oligomers. Evaporating off the solvent will leave the oligomer that can be weighed or alternatively the weight reduction of the film can be taken and the oligomer percentage calculated. Variations of this are to repeat the test after a period of time to give a measure of the rate of migration of the oligomers from the bulk to the surface. Other variations are to use different time scales and temperatures. Using mass spectrometry and chromatography also enables additional information to be gathered on the type of oligomer present in the extracts.

MHET; Monohydroxyethyl terephthalate,
BHET: Bishydroxyethyl terephthalate
B-2: Linear dimer,
C-2: Cyclic dimer,
C-3: Cyclic trimer,
TA: Terephthalic acid

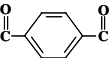
The volatility of the main monomers and oligomers that are generated from PET resin in descending order is: TA>BHET>MHET>C-3.

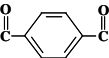
On the other hand, the amount of each in PET resin in decreasing order is: C-3>C-2>B-2>BHET>TA>MHET

The MHET amount being much smaller than BHET. BHET converts to MHET in air or when in contact with absorbed oxygen. BHET & TA are the main volatile substances in PET resins

	Melting Point °C
Cyclic dimer	175 224 229
Cyclic trimer (B type crystal)	319 317 - 320 321
crystalline transition temperature (A type - B type)	199 195
Cyclic tetramer	326
Cyclic pentamer	256

Figure 10 Typical cyclic oligomers found on PET



A = 

B = $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$

Structure	Molecular Weight	Melting Point °C
H[AB] ₁ OH	210.2	178
H[AB] ₂ OH	402.4	200 - 205
H[AB] ₃ OH	594.6	219 - 223
H[AB] ₁ -B-H	254.2	109 - 110
H[AB] ₂ -B-H	446.4	173 - 174
H[AB] ₃ -B-H	638.6	200 - 205
H[AB] ₄ -B-H	830.8	213 - 216
H[AB] ₅ -B-H	1023.0	218 - 220
HO-A-[AB] ₁ OH	358.3	>360
HO-A-[AB] ₂ OH	550.5	280 - 281
HO-A-[AB] ₃ OH	742.7	268 - 270
HO-A-[AB] ₄ OH	934.9	252 - 255
HO-A-[AB] ₅ OH	1127.1	233 - 236

Figure 11 Typical acyclic oligomers found on PET

It can be seen in the Figures relating to oligomers that the melting points of some oligomers is much lower than for the PET. In vacuum deposition, as the material to be deposited lands on the surface, there is a heat load from the latent heat of condensation as well as any heat load from the deposition source. Although the bulk film temperature may be kept low by the use of a chilled deposition drum the front surface temperature is higher. Thus it is conceivable that some oligomer may be volatilised during the deposition process. This acts in the same way as in a pattern metallisation process. Where the oligomers volatilise there will be either no or reduced deposition. In aluminium metallisation these will appear, when backlit, as pinholes where no aluminium has been deposited or as bright spots where there is reduced metallization. Where coating has successfully taken place on the oligomer the metal adhesion is likely to be low, as the oligomer will be poorly bonded to the PET surface, with low inherent strength and with low adhesion between the metal and oligomer. It is possible that this will lead to pickoff of spots of metal that will also, if the film is backlit, appear as pinholes.

CONCLUSION

If we consider the quality of the polymer film surface we can see that instead of the desired pure polymer surface it may actually be covered with polymer white powder and other particulate debris along with oligomers and other exuded additives. Atmospheric cleaning, by techniques such as ultrasonic pulsed electrostatic neutralised air or tack rolls, will remove most large debris from the surface but not exudates. Commonly there are problems of variable adhesion often blamed on poor plasma treatment. Initially the plasma treatment will have to be optimised for the particular grade of polymer film used. If a change of supplier is made and an equivalent grade used the surface may be different and the same plasma treatment may not produce the same results. Different suppliers may have a slightly different process and polymer composition including preferred additives, which will result in a different proportion and composition of exudates.

Where surface cleaning or treatments are done before the polymer enters the vacuum it is worth noting that contamination and exudates will be present on both sides of the web. A common fault is to treat only the side to be coated and following treatment to immediately re-contaminate the surface from the contact made during rewinding with the still contaminated back surface.

Ideally specifying a substrate material with limitations on the quantity of extractables as a way of helping to better define the incoming film quality.

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