Polyester (PET) Film as a Substrate: a Tutorial

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ABSTRACT

PET films are widely used as substrates for thin film vacuum deposition and many other coating processes. This paper is designed as a tutorial for users of PET films as a coating substrate. It will describe those parts of the chemistry, manufacturing processes, thermal properties, mechanical properties, chemical properties and web handling characteristics of PET that might be helpful for users. It will describe how many of the very useful properties of PET films result from the manufacturing process which, by its very nature, induces some degree of non-uniformity in the film properties. The paper will be particularly helpful for those who want or need to get to the next level of performance using PET as a substrate. The information has been culled from many sources as the author has been engaged in coating PET for 20+ years. There is a distinct bias towards vacuum coating, but PET users practicing other coating processes will also find value here.

INTRODUCTION

Polyester (PET) film is widely used a vacuum coating substrate because of its balance between a number of excellent properties and cost. It provides enormous utility for conventional applications and enormous potential for advanced applications. However the same materials and process issues that produce the excellent properties also generate a few challenging characteristics, including: variability, non-uniformity, and instability of attributes. This paper examines the materials and processes used to produce PET films (to improve our understanding of the origin of these properties) and collects data from a broad range of useful sources and references into one location.

PET is produced in large quantities (37 million tons in 2004, second in volume for polymer resins only to polypropylene), but two thirds is used for textiles and a quarter for bottles. The remainder is used for film and special items [1]. Another estimate puts the US use of PET for film at 7% of the US PET resin production [2]. PET <u>film</u>'s unusual balance of physical, chemical, thermal and electrical properties has made it valuable in a wide range of markets, including industries producing computer and video tapes, motors, capacitors, flexible circuitry, graphic arts material, release products, cards, labels and packaging [3]. For example one producer lists 87 distinct PET film grades on its web site [4]. Only a few of the many films available are used for vacuum deposition. Thus our application space is a small part of a much, much larger business, yet it benefits from the developments made in support of these other film and non-film applications through improvements in technology and reductions in cost based on economies of scale.

A summary of the development and current practice for production of PET resin is given in [1]. A brief history of PET films, the substantial corporate consolidations that occurred in the PET film business in the 1990's, and a summary of the size of the major producer's PET film businesses is given in [3] and [5]. More worldwide market information is available [6] with the US market broken down in detail in [2].

PET FILM

PET films are semicrystalline, relatively high melting, yet readily processible. The resin used for film is well suited for biaxial orientation, which in turn leads to outstanding properties. It has a well defined melting point and moderate molecular weight (typically 20,000 g/mol, which is equivalent to ~100 monomer units, for film applications). The melting point is low enough for good processibility and provides excellent rheology for polymer filtration and melt extrusion; yet it is high enough to provide films with excellent mechanical properties and low thermal shrinkage. The films exhibit inherent chemical and thermal stability which in turn permits recycling of polymer scrap (5-25%) – an economic plus. In some critical applications no recycled resin is used [7].

PET has a regular linear structure which leads to films with an ordered structure through chain orientation and crystallization. PET film is an imperfect two-phase system consisting of interconnected crystalline and amorphous domains with densities of 1.455 g/cm^3 and 1.333 g/cm^3, respectively. Typical films are approximately 50% crystalline with densities near 1.40 g/cm^3. The domain distribution depends on details of the film processing: stresses and temperatures. In general PET films are strong and thermally stable. No other material possesses both the excellent properties and low material cost of PET.

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PET FILM MANUFACTURING BASICS

Since this paper is addressed to users of PET film, a typical film manufacturing process will be described. There are many options and trade-offs available to the manufacturer. The typical process provides enough detail to illuminate the issues relevant to users. Excellent process schematics are given in [3], [7] and [8]. References are given for those who wish to go into more detail. This section is based largely on [3] and [7].

FILM EXTRUSION

The typical process starts with dried PET resin (<0.01 wt. % water) formed from the reaction of ethylene glycol plus terephthalic acid. Water is a reaction byproduct and must be removed. The resin is melted and extruded as a sheet onto a chilled drum designed to rapidly quench the resin to form an amorphous sheet of PET film. Any crystallinity at this stage will have negative consequences in subsequent stages. The melt is generally at 280-310 C° to minimize crystallization. Prior to extrusion the resin is filtered using sintered or non-woven metal disks (5-30 µm pore size). The filters are used to remove polymer gels and particulates, consisting of degraded polymer, catalyst residues, or pipe deposits. It is critical that the quenched film be formed with a high degree of thickness uniformity both down web and cross web. To insure down web uniformity the drum must be free of vibration and must rotate smoothly to provide thickness uniformity, and the extruder must be very uniform. To insure cross web uniformity, thickness measurements made near the end of the line are fed back to control to opening of the linear slot dies, using electrically heated die bolts to control the local thickness. To insure a smooth film surface the drum is highly polished, and the process uses electrostatic pining of the incoming molten sheet of resin to the drum to eliminate the entrapment of air bubbles. At this point the film is fully amorphous.

LENGTH ORIENTATION

The next stage involves stretching or "drawing" the film in the longitudinal direction or machine direction (MD). It is often referred to as length orientation (LO). The film is first heated to 85-90°C by contact with a heated roller. The film is then passed over rollers driven at higher speeds, resulting in the film being stretched, typically by a factor of 3-4. This results in stress induced uniplanar axial orientation in which the polymer chains become more aligned or crystallized. The temperature, strain, and strain rate act in combination to influence the rate and extent of crystallization in the film. After length orientation the film is 10-20% crystalline, and the film becomes stronger.

TRANSVERSE DRAW

The film is then passed through a long oven in which the film is stretched in the cross web or transverse direction (TD). To do this, the film is captured on its edges by clamps (or clips) attached to a moving chain. The lateral motion of the chain controls the stretching of the web. As the film enters the oven it is heated to above 100°C; typically the film is stretched in the cross web direction by a factor of 3-4. This stress induces further orientation of the polymer chains. The typical process results in film properties (tensile strength and elongation) that are "balanced," although balanced is an approximation, at best. The oven is often called the tenter or stenter oven. After the transverse draw the film is 25-40% crystalline.

HEAT SETTING

While the film is still in the oven, it is exposed to 180-230°C for several seconds. The film increases in crystallinity, and the non-crystalline regions undergo significant relaxation. The heat setting process may use three or more regions with independent control of the temperature and lateral stress to optimize the film's final properties [5]. This process stabilizes the structure of the film, which is now ~50% crystalline.

SLITTING

The edges of the film which were captured in the chain-mounted clips are very thick and are slit off before the film is wound into a roll. It is often possible to reuse material slit from the edge, improving raw materials usage and reducing film cost. The film's crossweb thickness profile is measured at this point and fed back to the extrusion dye to correct non-uniformities. Additionally the winder may be oscillated slowly in the lateral direction to minimize the build up of thicker regions of the web on the winding roll. This process doesn't improve the web thickness profile but reduces the impact of slight non-uniformities on the roll quality. The resultant film does exhibit some camber, and while the camber angle is small, it can affect tracking of the film in some critical applications.

HEAT STABILIZATION

For applications that require low thermal shrinkage, the standard film may be heat stabilized by passing through a high temperature off-line oven with the film at very low tension. Standard PET film will shrink by 1-3% after 30 minutes at 150°C. Following heat stabilization the shrinkage can be reduced to 0.1-0.2 % in the MD and less than 0.1% in the TD [3].

PET FILM PROPERTIES

The film process described produces rolls of PET film that have the properties required for a standard PET film, namely: high mechanical strength, good flexibility, excellent optical properties, flatness, dimensional stability, and a thicknesses of 0.6-500 µm. The thermal characteristics of PET film enable it to retain its physical, chemical, and electrical properties over a wide temperature range, with good resistance to the effects of heat ageing up to 150°C. The process of making biaxially oriented polyester film is complex and requires a detailed understanding of the interrelationship between polymer properties and process to give the desired final properties in the film. Each step has been carefully studied and modeled. Enormous process engineering resources have been expended in each step of the process; for details see [3].

Most of the molecules in the biaxial finished film are aligned in the plane of the film, creating regular crystalline regions and rendering good mechanical properties to the film. The film has a predominantly lamellar structure with low to very low z-direction strength. This structure has an impact on the peel adhesion for vacuum coatings: failure is often cohesive within the PET with the PET film fracturing between lamella. The evidence for this is a thin layer of PET often found on the film side of the peeled coating surface. A surface amorphization process for PET and other polymer films has been patented [9]. This process randomizes the polymer chains in the near surface layer and increases the apparent peel strength by increasing the work of adhesion as the failure locus is moved more deeply into the film.

It's important to note that PET films can be made with a broad range of properties depending on the details of the process but also that many of the important properties of PET films are not completely uniform. As a first example, consider the transverse or sideways draw process. The sheer scale of the equipment ought to make one question how the stretching process could be completely homogenous. Ideally one hopes for totally uniform temperatures and stresses. But as seen in Figure 1, there is a bow in the film stress caused by Poisson's ratio: as the film is stretched sideways it shrinks in the machine direction. This gives rise to nonuniformity in many mechanical properties: notably strength and thermal and humidity expansion. Not only are the properties different in the cross web and down web directions, but they vary depending on the position in the cross web direction. For many applications this is a non-issue, but it can be important some applications.

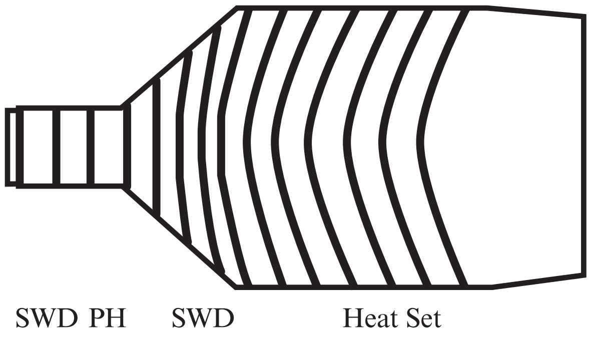

Figure 1: Development of the macroscopic bow in film. Abbreviations: SWD, sideways draw; PH, preheat. Adapted from [3].

In addition to the variability of the film attributes with direction and with position, it can also be noted that the film structure is to some degree metastable. Figure 2 compares the differential scanning calorimetry scans for a PET film sample (B) at the time of manufacture to that of one taken two years later (A). The trace shows a pronounced endothermic peak in the region of the T_g caused by the reduction in free volume over time.

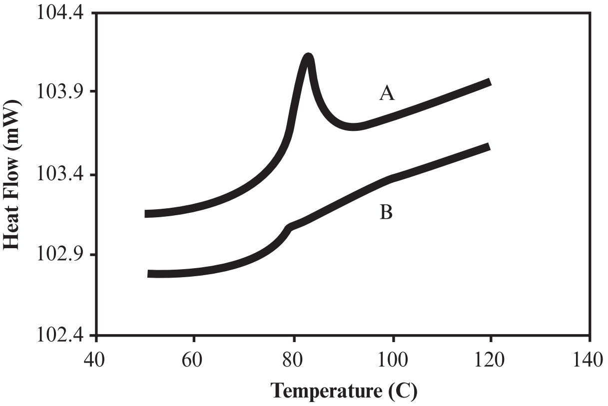

Figure 2: Differential scanning calorimetry (DSC) of commercial PET film [3].

A summary of the thermal properties of PET film is given in Table 1. Note that several values are given for each attribute. This is intentional and reflects variability of the material and the range of values typically reported for commercial PET films.

Table 1: The Thermal Properties of PET Films.

Property	Typical values
Melting point	254, 256, 258°C
Glass transition temperature	70, 78, 80°C
Service temperature	-70 to 150°C
Coefficient of thermal expansion	10, 12-20, 19x10-6 / K (from 20-50°C)
Specific heat	1300 J/kg-K (at 20°C) 0.28 cal/gm/K (20°C)
Thermal conductivity	0.13 W/m-K (up to 80°C)
Shrinkage	0-2 % (30 min at 150°C)
Shrinkage for "heat set" films	0.15% (30 min at 150°C)

The semicrystalline nature of PET results in low shrinkage below the heat set or heat stabilization temperature and higher shrinkage above that temperature. Some have suggested the PET will shrink at any temperature above its glass transition temperature (80°C). But in general that underestimates the stability of PET, especially if it is held under tension. An unsupported film may curl above 80°C, but during vacuum coating with the film under tension, the glass transition temperature can be exceeded without major difficulty.

The coefficient of thermal expansion for PET is lower than that of many polymers; as noted above it is not isotropic and depends strongly on the orientation process. It can differ by more than a factor of two for measurements on the same sample taken in differing directions. Many of the thermal and mechanical properties depend on orientation in the substrate. An excellent discussion of these issues and the effects of annealing PET films are given in [10].

Shrinkage is time and temperature dependent and results from a relaxation of strains induced in processing. Once a film has shrunk at a particular temperature, there is little further shrinkage as long as that temperature is not reached. Thus total shrinkage is virtually path independent. Figure 3 shows the time dependence of shrinkage for a standard PET film at three selected temperatures.

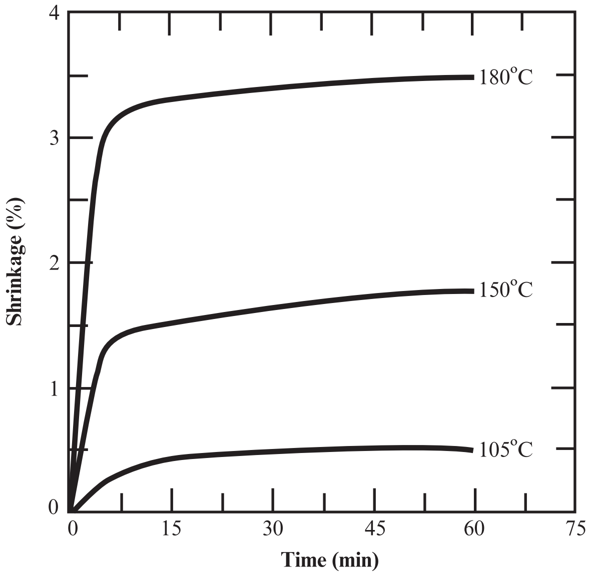

Figure 3: Unrestrained shrinkage of PET film heated in air [7].

Figure 4 shows the MD and TD shrinkage versus temperature after a 5 minute exposure for standard and heat stabilized versions of the same film. Note the differences between the shrinkage in the two directions. It is typical that the TD shrinkage is smaller than the MD shrinkage. Thus if only one value for shrinkage is reported, the more attractive TD value is likely being reported.

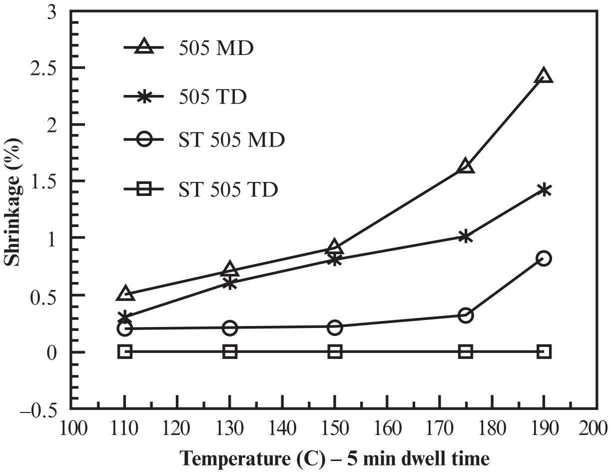

Figure 4: Shrinkage of PET as a function of temperature in the machine direction (MD) and the transverse direction (TD) for a standard PET film (505) and its heat stabilized version (ST505) [11].

In modeling the cooling of a PET film substrate (i.e., during deposition), the heating time and the thermal time constant define whether a steady state or a transient model should be used. For the case of a film initially at uniform temperature and followed by instantaneous increase of the temperature of one surface by ΔT, the thermal time constant, $T_{1/2}$, is the time it takes for the temperature of the cooler surface to rise by $\Delta T/2$ and goes as the square of the film thickness. Using typical values for PET, Table 2 gives the thermal time constant for several thicknesses of PET. For comparison the total coating time during evaporation at 2000 fpm with 12" aperture = 30 msec, and the coating time during sputtering at 20 fpm with a 12” aperture = 3 sec.

Table 2: Thermal time constant ($T_{1/2}$).

Thickness (μm)	Time constant (msec)
12	8
25	35
50	140
100	550

The mechanical properties of PET film are presented in Table 3. PET retains its physical properties, including tensile strength, folding endurance and tear strength over a wide temperature range (-70°C to 150°C). The film is tough and has high tear initiation strength. PET film does not contain plasticizers (this is a key advantage in the area of packaging of consumable items) and does not become brittle with age under most conditions [3].

Table 3: Mechanical Properties of PET Films.

Property	Typical values
Density	1.39, 1.40 g/cm3
Young’s modulus	4.5, 4.9 GPa at 25°C 1.4 GPa at 120°C
Poisson’s ratio	0.37-0.44
Oligomer content	1.3-1.8 wt %
Refractive index	1.576
Hygroscopic coefficient of linear expansion	6, 7, 8, 11, 12 x 10-6 / % RH
1 lb/in-mil (1000 psi)	ΔL/L = 0.15%
ΔT = 100 C	ΔL/L = 0.12-0.2%
ΔRH = 100%	ΔL/L = 0.12%

PET has high modulus, 2-3X higher than amorphous polymers. Since film handling ease goes as the film stiffness, the modulus times the cube of the thickness, PET is relatively easy to handle. Typical winding tensions for good roll quality are of order 500 psi (0.5 lb tension / in width * mil thickness) [12]. Higher winding tensions may lead to roll formation problems. Tensions in the coating zone may be much higher (2900 psi) [13]; the highest coating tension this author has seen reported was 7000 psi [14]. A useful rule of thumb, to stay in the elastic range (with no permanent distortion) is to stay below 0.5% elongation or ~3300 psi for PET. Note that a Poisson’s ratio of 0.4 implies that the tension needed to produce 0.5% downweb elongation also produces 0.2% crossweb shrinkage. It can be useful to pre-stretch film in the cross web direction with bowed rollers before the coating zone.

The modulus decreases with increasing temperature with a form that depends on the particular grade of PET and its processing history, Figure 5. While this loss of modulus suggests major problems due to heating in the coating zone, recall that if the film is on a chilled drum, with the hot zone adjacent to much cooler zones also on the drum, the segments of the film in cooled zones isolate the film in the hot zone from the externally applied tension.

Another view of the temperature dependence of the modulus is given in Figure 6. Note that for a 12 micron thick PET film, 20.5 kg/m = 0.5 lb/in-mil. Thus an unsupported film heated to 90 C would likely see unacceptable film extension at nominal film tensions.

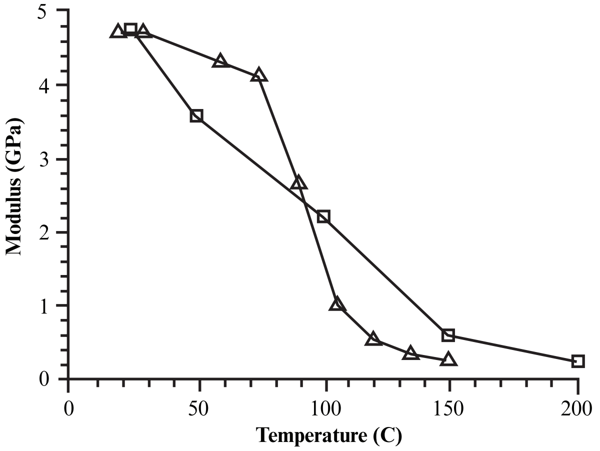

Figure 5: Temperature dependence of the elastic modulus for polyester produced by different manufacturers [13].

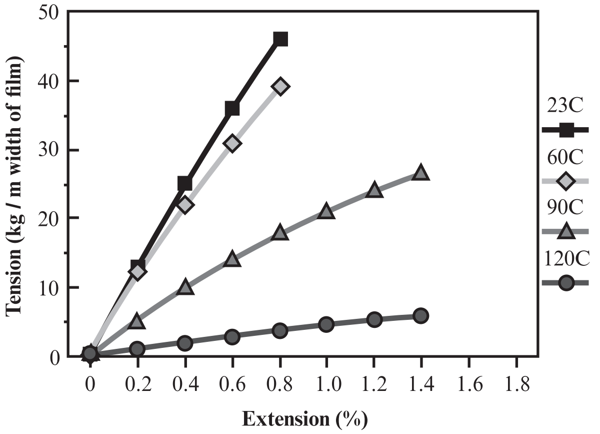

Figure 6: Typical stress/strain curves for 12 micron PET film [15].

If dimensional stability is important in your application, note from Table 3 that the extension (ΔL/L) for a nominal tension level is comparable to the extension for a temperature change of 100 C° or a change in humidity level of 100% RH. The latter is particularly important if wet chemical processing (100% RH) is used in tandem with vacuum coating (0% RH). The topic of dimensional stability as it is related to moisture pick-up has been discussed carefully for PEN films [16] and [17]. The trends are similar for PET. At ambient temperature, the time constant for equilibration is very long (hours). At 150°C, the time constant is a few minutes. Water absorption in PET has been reported in various manufacturers’ data sheets over a broad range of values, including 0.14%, 0.4%, 0.5%, and 0.75%.

The effects of temperature on moisture release under vacuum (outgassing) have been treated previously [18]. A simple diffusion model was shown to be appropriate. Figure 7 show the results of a calculation assuming a diffusion constant of $2\mathrm{x}10^{-5}$ m^2/sec and an activation energy of 40 kJ/mole for a "typical web material." Measurements of the diffusion constant for water in three different commercial PET films have been reported as 1.6-$2.2\mathrm{x}10^{-5}$ m^2/sec [19]. This plot reinforces the large change in time constant for moisture level changes in PET with temperature.

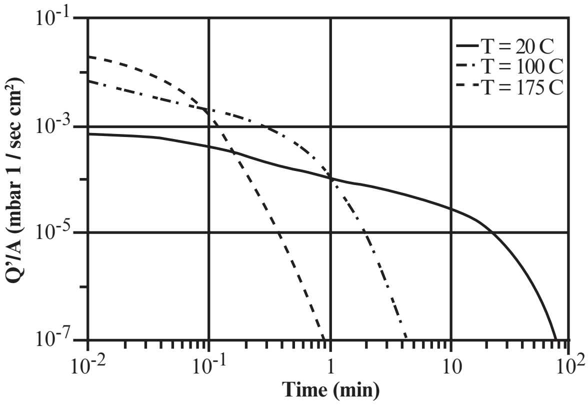

Figure 7: Diffusion dominated outgassing of 100μm polymer web at constant temperatures of 20, 100, and 175°C.

PET is unusually resistant to creep: 0.1% after 260 hours at 2980 psi and 0.2% after 1000 hours at 3000 psi (3 lb/in-mil) both at room temperature; 0.9% after 4000 hours at 500 psi at 100C. PET has a shear resistance that is significantly higher than other polymer materials, implying that die cutting, punching, and tear initiation may more be challenging. PET has excellent "profile" [20]. Profile is a measure of the uniformity in thickness in the cross web direction. It permits good roll quality and film handling.

MISCELLANEOUS PROPERTIES

PET has moderate to good chemical resistance [5]. It can be dissolved in hexafluoro-2-propanol, m-cresol, o-chlorophenol, trifluoro-acetic acid (spin cast PET films have been made for research purposes from the latter two solvents [21]). It is attacked by strong acids and bases, but is durable to hydrocarbons, chlorinated hydrocarbons, dilute acids, alcohols, esters, ethers and ketones. It is not recommended for outdoor use or with hot water. It has low moisture permeability and good resistance to staining. Polyester has oxygen in its backbone and thus provides fair to good adhesion for metals and metal oxides. Corona treatment is not uncommon, though its treatment effects deteriorate with time. Untreated PET has a surface energy of 42-46 dyne/cm; corona treatment yields 54 dyne/cm and above. There have been several reviews of vacuum based surface modification techniques [22].

PET has excellent optical transmission in the visible from 400-700 nm. Clear films can be 88% transmitting. PET is optically birefringent and thus unsuitable for traditional LCD displays.

ADDITIVES TO PET

There are a number of additives used in producing PET films, including catalysts, slip agents, and surface coatings.

Producing useful PET resin requires the use of efficient catalysts since the uncatalyzed reaction is slow. Antimony compounds have been the catalysts of choice in most PET plants since its invention. A good summary of PET reaction and polymerization chemistry is given in [1]; more details are given in [23]; recent developments are described in [24]. Many catalyst systems are used, but as one example, manganese acetate is used to catalyze the formation of the "monomer." Phosphoric acid is added as a stabilizer to neutralize the manganese catalyst and prevent color formation during subsequent processing. The monomer is polymerized using antimony oxide because it gives a good balance of catalytic activity in the presence of the phosphorus based stabilizer and cost. Sometimes cobalt is added to mask the inherent yellow color of polyester. These additives are usually present in the range of a few tens to a few hundred parts per million in the finished film. They are found as inorganic particles which can be up to sub-micron in size. These particles can affect the clarity of the film and can also contribute to surface roughness. High clarity films are produced using care to minimize the undesired effects of these additives.

PET films almost always have at least one surface "roughened" either by the addition of slip agents or by a surface coating. For films less than 50μm thick, slip agents are added for good winding and handling. Films greater than 50 μm may or may not have slip agents depending on the clarity required. The absence of slip additives implies high coefficient of friction, potentially poor web handling, and possible blocking, bonding of adjacent layers of film. Some no-slip thick PET films are mechanically knurled at the edge for handling. The slip agents are typically inorganic particulates added to the resin before casting. These can be added through the entire film or can be added to just one surface by casting a dual layer film. In more complicated constructions, multilayer films can be produced with different types or quantities of slip agents added to each surface layer. Coarse particles scatter light, affect optical properties, and produce rougher surfaces. Migratory slip agents are rarely used in PET. High humidity and/or high temperatures aggravate blocking.

PET films are often coated during manufacturing to produce surfaces more receptive to subsequent coatings. Planarizing coatings may be used [25]. The details of these coatings are often treated as proprietary by the various film manufacturers and because of this can be changed without full notification to a customer. While a change may not affect all customers, it can occasionally impact adhesion or durability of a vacuum deposited coating (since the latter are often quite sensitive to the details).

OTHER ISSUES

The slitting of the thick edge at the end the film line is usually not the last slitting operation before it comes to our coaters. Slitting operations invariably generate particulate debris. A good summary of slitting and other particulate defect sources, defect counting, and prevention and cleaning is given in [26]. It is also important to note that the polymerization reaction to form PET also produces low molecular weight species. The most common is the "cyclic trimer," consisting of three monomer units. Unless special care is used, the trimer level in PET films is found to be 1-3 wt % [27]. As the film is heated the trimer can migrate to the film surface and nucleate as particles. Note that 0.5 µm trimer particles can appear after 10 minutes at 100C°. Smaller particles may be formed at lower temperatures and/or shorter times but are difficult to image. Larger particles (much larger) occur after longer times and higher temperatures. A continuous coating on the PET surface usually precludes the nucleation of particles but scratches or coating defects may permit trimer particle formation. Oligomer particle generation is significantly lower in PEN than PET under many conditions.

BOTTOM LINE

Defining the best film choice for a particular new application can be complicated: partnering with your film supplier can be an enormous benefit. As one film producer has remarked, "this is a fast evolving field and the results discussed in the literature may not represent what the flexible substrate supplier would (or will in the future) present as their preferred tailored [substrate] candidates" [28]. But also realize that a film manufacturing run performed under special conditions for a small volume can be an enormously inefficient use of a very expensive manufacturing facility and hard to justify.

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