

2. Primers and tie-coats
3. Adhesion promoters
  - a. covalent bonding
  - b. chemical similarity
  - c. other forces of attraction - hydrogen bonding, electrostatic, van der Waals
4. Corona and plasma treatment
5. Surface roughening

#### A. Solvent and co-solvent composition of the coating fluid:

Plastics of low surface energy present difficult surfaces for coating adhesion. Also, as discussed above, plastics may have a polymer conformation that is not conducive to good coating adhesion. To accommodate these types of plastics, one approach to promoting adhesion is through careful formulation of the coating composition. In doing so, significant emphasis should be given to the balance of solvents and/or cosolvents used in the formulation. Consideration of the demands of environmental regulations, to reduce volatile organic compound (V. O. C.) usage, presents a significant challenge to the formulator.

The primary action that must take place is to relax or partially solubilize the surface polymer molecules, thus, providing the potential for coating polymer or binder resin to penetrate the plastic surface and form an interpolymer entanglement. Temperature will also improve this action, especially if the temperature can be elevated to a point well above the  $T_g$  of the plastic without detrimental effects on the plastic or coating composition. This solvent/temperature action will result in exceptional adhesion of the coating.

In practice, the formulator must consider the solubility parameters of the solvent used in the coating composition and both the coating polymer or binder resin and the plastic or polymer substrate. Solubility parameter theory<sup>3</sup> provides numeric three dimensional coordinates for solvents according to Equation 4.

$$\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \text{Eq. 4}$$

Where:

$\delta_o$  = Solubility parameter

$\delta_d$  = Component due to dispersive forces

$\delta_p$  = Component due to polar forces

$\delta_h$  = Component due to hydrogen bonding

It is, however, common practice to use only a two dimensional approach to permit easy plotting of parameter coordinates according to standard X-Y graphing. The most frequently used parameters used in such plots are the polar ( $\delta_p$ ) and the hydrogen bonding ( $\delta_h$ ) according to the Hansen solubility parameter theory<sup>3</sup>. A solvent will be located at a specific point according to its parameter value, but polymers will have a range of solubility and will cover an area within a plot of  $\delta_p$  vs.  $\delta_h$ . The center of the polymer solubility area may be designated the solubility parameter average and may be used to determine those solvents that are most likely to exhibit high potential for dissolution of the polymer based on proximity to the polymers' average value.

Also it is important to recognize that binary, tertiary, etc. mixtures or blends of solvents will exhibit a summed solubility parameter value based on the weight fraction of each solvent in the mixture according to Equation 5.

$$\delta_{O \text{ mixture}}^2 = \sum_{i=1}^n W_i \delta_{di}^2 + \sum_{i=1}^n W_i \delta_{pi}^2 + \sum_{i=1}^n W_i \delta_{hi}^2 \quad \text{Eq. 5}$$

Where:



$W_i$  = Weight fraction of solvent i

$\delta_{di}$  = Component due to dispersive forces of solvent i

$\delta_{pi}$  = Component due to polar forces of solvent i

$\delta_{hi}$  = Component due to hydrogen bonding of solvent I

And:

$$\delta_{p \text{ mixture}} = \sum_{i=1}^n W_i \delta_{pi}$$

$$\delta_{h \text{ mixture}} = \sum_{i=1}^n W_i \delta_{hi}$$

will provide the parameters for two dimensional plotting of the solvent mixture or blend. Furthermore, as the solvent mixture of the coating composition begins to evaporate during drying and cure, the parameter values will shift in the direction of the solvent(s) having the lowest rate of evaporation. This leads to a very important realization. The solvent having the lowest rate of evaporation (the last one out of the coating during drying) should be a very good solvent for the coating polymer or binder resin and for the polymer constituting that of the plastic substrate. This will promote the best conditions for coating adhesion.

One last concept in the use of solvents is the fact that, as solvent evaporation progresses during drying, the surface tension of the coating or fluid layer may drift and present problems with uniformity and adhesion. Consideration of the surface tension of the solvent of lowest rate of evaporation is also important to maintain the optimum coating performance.

#### B. Primers and Tie-Coats:

There are many times where the coating chemistry desired will never be compatible with the plastic surface, even in consideration of the solvents used. Under these circumstances, primers or tie-coats serve to act as an intermediate layer for adhesion purposes. The basic premise is to apply a coating to the plastic surface that exhibits good adhesion and will also act as a compatible intermediate surface for the final topcoat composition.

It is often seen that primers and tie-coats can be specific for the type of topcoat composition to be applied to a particular plastic. "Universal" primers have been claimed with some materials but caution is warranted when examining them for any application.

Primers may be clear or filled to provide added surface area or roughness for maximum adhesion. Tie-coats are typically clear and may simply be an adhesion promoting agent solubilized or dispersed in low concentration in a particular solvent or water. These will be addressed in the next section.

#### C. Adhesion Promoters:

Adhesion promoters may be added to either the primer, tie-coat, or coating compositions and are primarily of three main types, those that bond covalently, those that bond by other forces of attraction, and those that promote adhesion by chemical similarity ("like-sticks-to-like"). In all instances, these types of adhesion promoters use the described mode of adhesion to the plastic substrate. They all, additionally, possess specific functional groups that are presented to the coating for subsequent bonding or binding of that layer. In application, it is typical to use a very low concentration of an adhesion promoter, thus, providing a near mono-molecular layer over the surface of the plastic. Effectiveness may decrease with greater applied thickness of the adhesion promoter. It is, therefore, essential to fully discuss and/or review the performance mechanism of the adhesion promoter through respective vendor communications.

In the use of adhesion promoters, the adhesion promoter must look for chemical functionality in the plastic to bond or bind to. With thermoset surfaces, the best performance of an adhesion promoter will be when there is a fair level of residual functionality remaining and available for binding. Polymers of low or no residual



functionality will remain more problematic to promote adhesion, but nonetheless, there are some options available.

A very popular class of adhesion promoters are silanes and several are available for specific combinations of plastics and coatings. For these types of adhesion promoters to find such functionality certain conditions must be met<sup>4</sup>. First, the plastic must have appropriate functional groups. Second, the adhesion promoter must be mobile enough in the primer or coating composition for the time necessary to migrate to and find the appropriate functionality on the surface of the plastic. This implies careful formulation of the solvent balance of the coating composition and an appropriate surface activity in the adhesion promoter itself. Third, there should be minimal competition between the plastic functionality and the coating polymer or binder resin so that the effectiveness of the adhesion promoter is not diminished. Fourth, the adhesion promoter must be soluble in the coating composition and miscible with the polymer of the plastic.

Of the types of plastics available, polyolefins and other hydrocarbon thermoplastics are difficult substrates for coating adhesion. When dealing with these substrates, polychlorinated polyolefin adhesion promoters<sup>5</sup> have been used to bind the coating to the plastic surface by their chemical similarity. Additionally, being relatively hydrophobic, they tend to migrate to the coating/substrate interface and orient themselves with their pendant maleic anhydride and/or halogen groups toward the coating layer.

#### D. Corona and Plasma Treatment;

Corona and plasma treatment of plastic surfaces causes a change in the chemical nature of the surface through possible oxidation or possible microstructure formation so that subsequent coating adhesion is made maximum. These treatments are quite effective for a number of types of plastics and work well for most types of coatings. In particular, this form of treatment works remarkably well for polyester, polyolefin, and other hydrocarbon thermoplastics.

Corona discharge is made possible by high voltage across a gap through which the plastic substrate is passed. Current passes from an electrode to a grounded hardened steel support surface for the plastic. This hardened steel support may be ceramic coated for longer use. Plasma discharge is, in simple terms, a high temperature flame impinging on the surface of the plastic for a very short period of time. The effectiveness is not necessarily permanent and it is best to apply the desired coating shortly after treatment.

#### E. Surface Roughening:

As introduced earlier, rough surfaces are easier to coat and to adhere to. Although, the surface tension of the base plastic material does not change, microscopically the surface has varied angles causing the net contact angle that the coating makes appear exceptionally low. The increase in surface area coated also contributes to adhesion. When this option is acceptable in the overall process of producing the plastic article, it is advised to take advantage of it, especially in combination with other forms of adhesion promotion.

### Summary

By no means are the concepts introduced above all inclusive for what the formulator needs to know about plastic surfaces for successful coating design. There are numerous other concepts and principles that interplay with the science of coating design for plastics. Obstacles always seem to occur, some of which may be insurmountable. If the coating cannot be modified to comply with requirements, perhaps the type of plastic can. It is always helpful to combine a coating formulators skill with that of a polymer or plastic engineer to design the best possible end product. The plastic coating formulator must always realize that the product is never a fluid composition but always an article composed of a coated plastic. The coating and the substrate must function synergistically as a unit to satisfy the requirements of the final consumer.

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**About the Author**

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The surface energy of a packaging film, often times referred to as the “dyne” level (dynes/cm) is a critical film property when printing, coating or laminating packaging films. The main objective of any surface treatment method is to increase the surface energy of the film surface to improve wet-out and adhesion of coatings, inks and adhesives used in converting the film into packaging. Typical polymers used for packaging films will naturally have a surface energy without surface treatment anywhere from 29 to 45 dynes/cm. A typical rule of thumb to insure good wet-out and adhesion to a substrate is that the surface energy of the substrate should be 7-10 dynes/cm higher than the surface tension of the coating being applied. As an example water has a surface tension of 72 dynes/cm compared to the surface tension of methanol which is 22.6 dynes/cm. The surface energy of a polyester film is approximately 42 dynes/cm thus allowing the methanol to easily wet-out the surface of the polyester, however the water (~72 dynes/cm) which is 50 dynes higher than the methanol will bead up, not wetting out the polyester film.

There are several different ways of surface treating a film to increase the surface energy thus improving wet-out and adhesion of various coatings, inks and adhesives. Corona discharge, flame treatment, priming and chemical etching can be used, typically individually, to increase the surface energy of a packaging film. These treatment methods can be effective if used correctly.

## Priming

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Priming film to increase surface energy and improve adhesion of a coating, ink or adhesive often times is done in conjunction with corona treatment. The film is corona treated to increase the surface energy enough to provide good adhesion for the primer coating to the film. A primer is selected that will provide a high surface energy for good adhesion and possibly improve the surface texture of the film. This method can increase the cost of the film greatly.

## Chemical Treatment

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Chemical treatment of a film typically involves cleaning, etching and rinsing steps. The cleaning removes any surface contaminants. The etching involves the use of an acid, base or oxidizing agents such as nitric acid ( $\text{HNO}_3$ ) or potassium chromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) to chemically change the polymer surface. Finally the film is rinsed clean of the etching chemicals and dried. This process is usually done following film manufacturing, which significantly adds to the final cost of the film. This treatment method is often slow and creates waste disposal issues.

## Flame Treatment

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Flame treatment involves the use of a burner unit that generates a flame with a specific plasma value (PV) ratio or fuel to oxygen ratio. The film passes directly through the flame tips, which have formed an oxygen rich plasma thus treating the surface of the film in contact with the flame. This treatment method is said to produce high surface energy levels and longer lasting treatment levels. In the past this method was considered dangerous due to the presence of a long open flame., However, improvements in equipment design and controls have greatly reduced the hazards.

A flame treatment study was conducted on biaxially oriented Ingeo film to evaluate the maximum obtainable increase in surface energy and the length that the film can retain the increased surface energy. An Ingeo film that had not been previously corona or flame treated was tested for the effect of burner gap, plasma value (PV), line speed and burner output to determine the best settings to obtain the maximum increase in surface energy. In addition, samples of the flame treated film were stored and tested over time to determine how long the film will hold the high surface energy level.



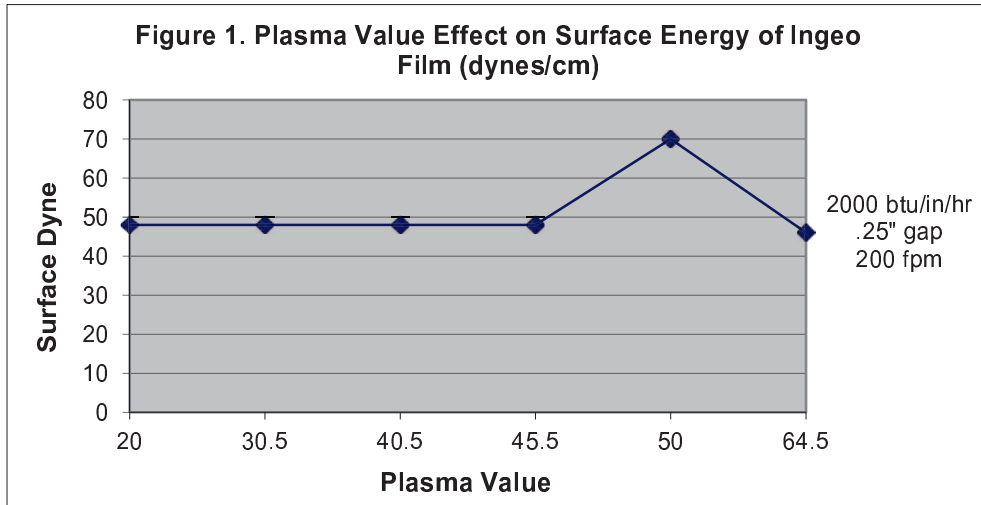


Figure 1 shows that a plasma value of 50 obtains the highest surface energy level (>70 dynes/cm) for the Ingeo film. A plasma value of 50 is considered to be a 1:1 ratio of fuel to oxygen and a 10-point shift in this value represents a 1% change in the fuel to oxygen ratio. As an example a plasma value of 40 signifies a fuel to oxygen ratio that has a 1% excess of oxygen. Most packaging films used for flexible packaging achieve the highest surface energy when flame treated with a plasma value of 45, representing 0.5% excess oxygen in the fuel mixture.

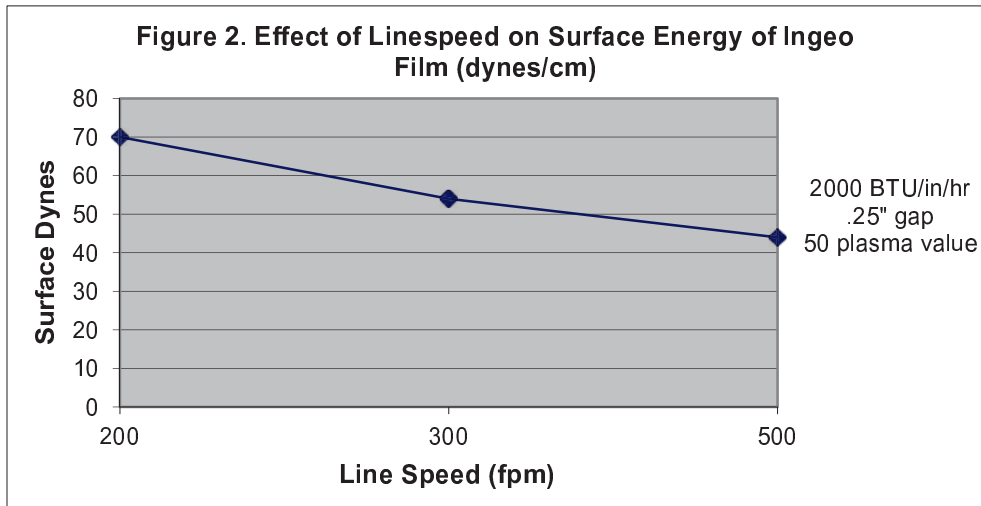


Figure 2 shows that when the line speed increases, the surface energy drops when using a fixed burner output and burner gap. This indicates that the burner output must increase as the line speed increases to maintain a high surface energy and subsequently the burner gap must be increased to prevent the film from distorting from the heat of the flame.



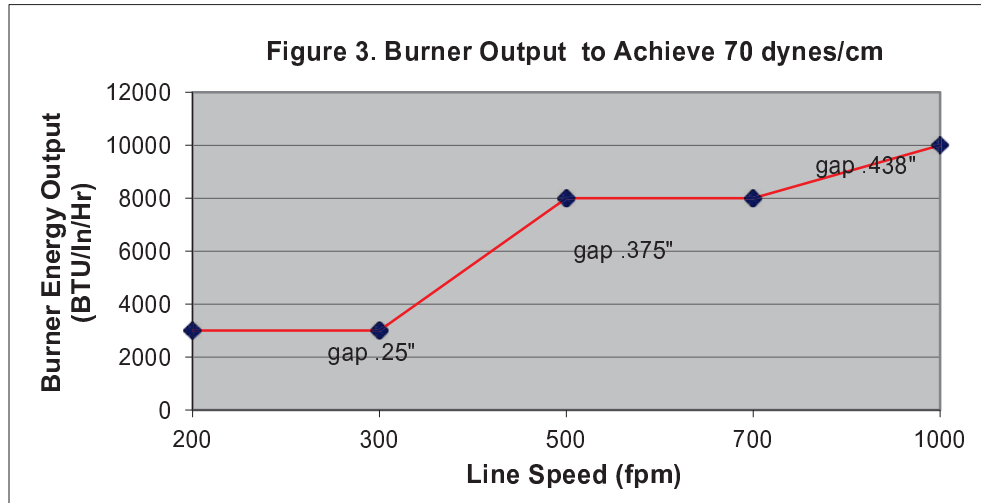


Figure 3 shows the relationship between line speed and burner output to maintain a surface energy of greater than 70 dynes/cm on BOPLA film.

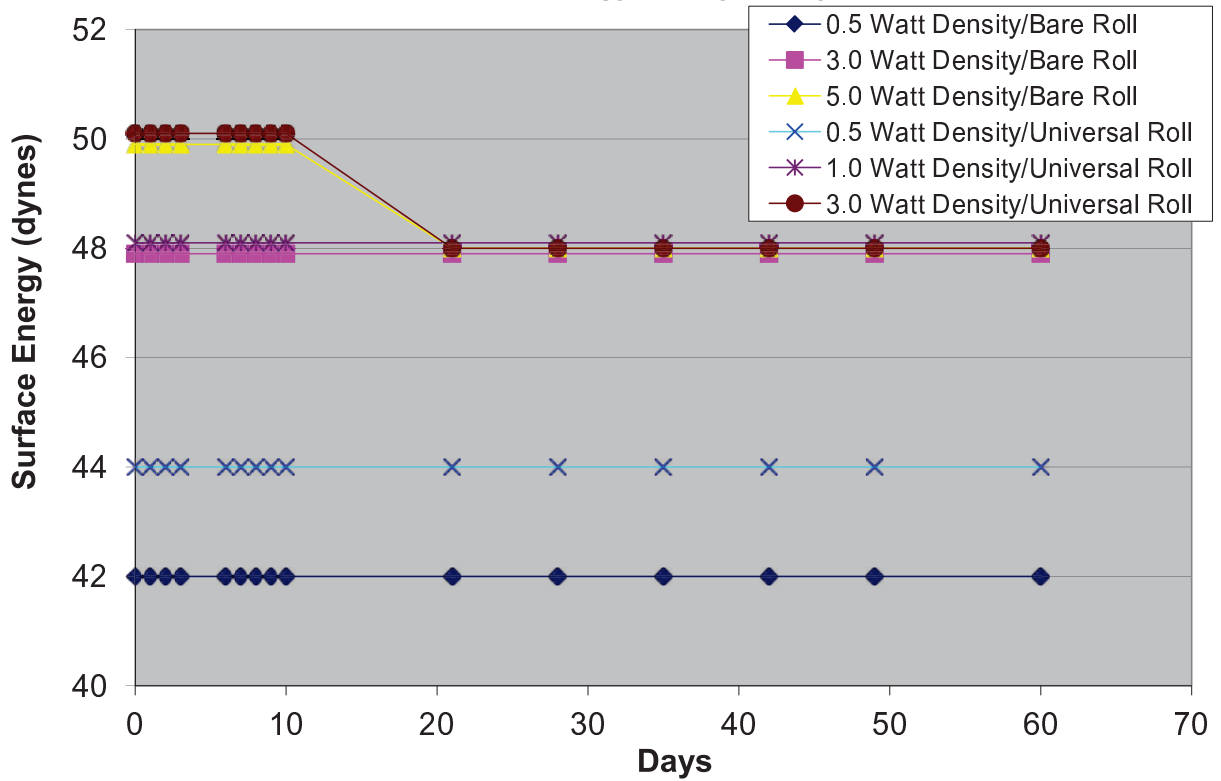
### Corona Treatment

Corona treatment consists of a high voltage electrical discharge across a fixed air gap between an electrode and a dielectric, usually a roller for web treatment applications. This discharge forms a corona in the gap between the electrode and the dielectric roller, thus treating the film surface toward the electrode. Treatment typically will decay over time and is adversely effected by high humidity conditions. Corona treatment is often done during film manufacturing and can be done again in-line with a secondary converting process such as printing to “bump” the film surface energy. This treatment method is user friendly, can be run at high line speeds( in excess of 1000 feet per minute) and can be controlled by the line speed to control the final treatment level.

A corona treatment study was conducted on Ingeo film to evaluate the increase in surface energy and the length that the film can retain the surface energy increase. Both Ingeo film that was corona treated during manufacturing and film that had no previous treatment were evaluated for discharge energy (watt density watts/square area) verses measured surface energy and the length of time in days that the film retained the surface energy. Figure 4 shows that very little watt density (1.0 watt density using a “universal roller”) needs to be applied to the treated Ingeo film to effectively “bump” treat the film to a surface energy of 48 dynes or higher. Unlike PP film, Ingeo film that has not been corona treated during film manufacturing can be corona treated effectively at a later date.



**Figure 4.**  
Initial Corona Treatment of BOPLA Film  
Surface Energy Decay Study



**Figure 5.**  
"Bump" Corona Treatment of BOPLA Film  
Surface Energy Decay Study

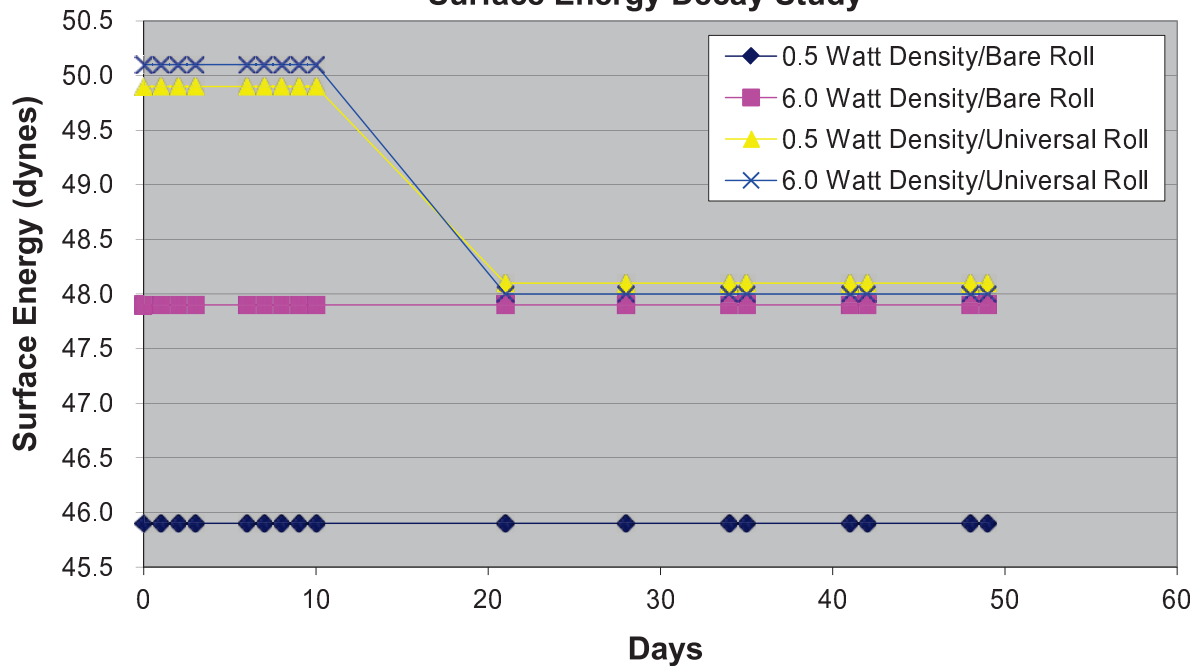


Figure 5 shows untreated Ingeo film does require more watt density to effectively increase the surface energy when compared to "bump" treatment, but not an unreasonable amount of watt density is required to be effective.



## Safety and Handling Considerations

Material Safety Data (MSD) sheets for Ingeo biopolymers are available from NatureWorks LLC. MSD sheets are provided to help customers satisfy their own handling, safety, and disposal needs, and those that may be required by locally applicable health and safety regulations, such as OSHA (U.S.A.), MAK (Germany), or WHMIS (Canada). MSD sheets are updated regularly; therefore, please request and review the most current MSD sheets before handling or using any product.

The following comments apply only to Ingeo biopolymers; additives and processing aids used in fabrication and other materials used in finishing steps have their own safe-use profile and must be investigated separately.

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Ingeo biopolymers have a very low degree of toxicity and, under normal conditions of use, should pose no unusual problems from incidental ingestion, or eye and skin contact. However, caution is advised when handling, storing, using, or disposing of these resins, and good housekeeping and controlling of dusts are necessary for safe handling of product. Workers should be protected from the possibility of contact with molten resin during fabrication. Handling and fabrication of resins can result in the generation of vapors and dusts that may cause irritation to eyes and the upper respiratory tract. In dusty atmospheres, use an approved dust respirator. Pellets or beads may present a slipping hazard. Good general ventilation of the polymer processing area is recommended. At temperatures exceeding the polymer melt temperature (typically 170°C), polymer can release fumes, which may contain fragments of the polymer, creating a potential to irritate eyes and mucous membranes. Good general ventilation should be sufficient for most conditions.

Local exhaust ventilation is recommended for melt operations. Use safety glasses if there is a potential for exposure to particles which could cause mechanical injury to the eye. If vapor exposure causes eye discomfort, use a full-face respirator. No other precautions other than clean, body-covering clothing should be needed for handling Ingeo biopolymers. Use gloves with insulation for thermal protection when exposure to the melt is localized.

## Combustibility

Ingeo biopolymers will burn. Clear to white smoke is produced when product burns. Toxic fumes are released under conditions of incomplete combustion. Do not permit dust to accumulate. Dust layers can be ignited by spontaneous combustion or other ignition sources. When suspended in air, dust can pose an explosion hazard. Firefighters should wear positive-pressure, self-contained breathing apparatuses and full protective equipment. Water or water fog is the preferred extinguishing medium. Foam, alcohol-resistant foam, carbon dioxide or dry chemicals may also be used. Soak thoroughly with water to cool and prevent re-ignition.

## Disposal

DO NOT DUMP INTO ANY SEWERS, ON THE GROUND, OR INTO ANY BODY OF WATER. For unused or uncontaminated material, the preferred options include recycling into the process or sending to an industrial composting facility, if available; otherwise, send to an incinerator or other thermal destruction device. For used or contaminated material, the disposal options remain the same, although additional evaluation is required. (For example, in the U.S.A., see 40 CFR, Part 261, "Identification and Listing of Hazardous Waste.") All disposal methods must be in compliance with Federal, State/Provincial, and local laws and regulations.

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Generally speaking, lost pellets are not a problem in the environment except under unusual circumstances when they enter the marine environment. They are benign in terms of their physical environmental impact, but if ingested by waterfowl or aquatic life, they may mechanically cause adverse effects. Spills should be minimized, and they should be cleaned up when they happen. Plastics should not be discarded into the ocean or any other body of water.

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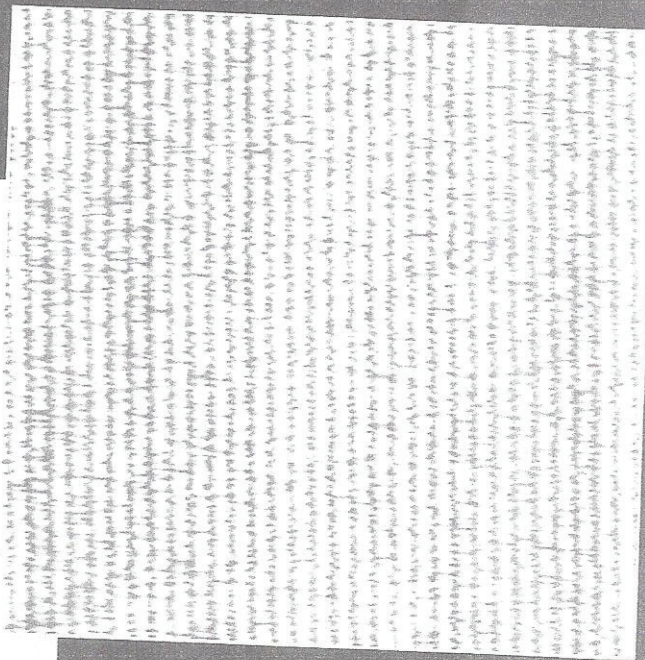
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# 7

## Adhesion Properties of Fluoropolymers

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### 1 INTRODUCTION

Adhesion properties of substrates are determined by the chemical nature of the surface, the topography and the cohesive strength of the surface regions. The chemical nature of a surface determines two critical factors in adhesion, namely: the wetting by a liquid component, and the forces of interaction across an interface where wetting has occurred.

The relative surface energies of the solid and liquid determine the degree of wetting. In general, a liquid will exhibit a zero contact angle, i.e. will wet a substrate, when the surface energy of the solid is greater than the surface tension of the liquid. Surface energies are determined by the nature of chemical groups (see Table 7.1). The chemical groups also determine the type of interactions

**Table 7.1.** Surface energies and polar and dispersion components of surface energy of some polymers[2]

Polymer	Chemical structure of monomer compared with ethylene	$\gamma_s^d$ (mN/m)	$\gamma_s^p$ (mN/m)	$\gamma_s$ (mN/m)
Polytetrafluoroethylene	4H replaced by F	18.6	0.5	19.1
Polytrifluoroethylene	3H replaced by F	19.9	4.0	23.9
Poly(vinylidene fluoride)	2H replaced by F	23.2	7.1	30.3
Poly(vinyl fluoride)	1H replaced by F	31.3	5.4	36.7
Low-density polyethylene	—	33.2	—	33.2

Key:  $\gamma_s^d$  Dispersion component of surface energy;  $\gamma_s^p$  polar component of surface energy;  $\gamma_s$  total surface energy.

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## Determining Critical Surface Tension of Solid Substrates

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The ease in which an adhesive or sealant wets (makes intimate contact) a substrate surface and the work necessary to separate the adhesive from the substrate can be related to the surface energies of the adhesive, substrate, and subsequent interface. In an ideal situation for spreading or wetting, the surface of the substrate should always have a higher surface energy than that of the liquid adhesive<sup>1</sup>. Surface energy,  $\gamma$  (gamma), is used interchangeably with the terms "surface free energy" and "surface tension".

The surface energies of liquids are readily determined by measuring the surface tension with a duNouy ring. A clean platinum ring is placed under the surface of the test liquid, and the liquid is slowly moved downward until the ring breaks through the liquid surface. The force is recorded, and by means of appropriate conversion factors, the surface tension of the liquid is calculated. There are several other common methods described in the literature for measuring the surface tension of liquids.

However, the measuring of surface tension is not as straight forward when it comes to solid surfaces. Direct surface tension measurements on solids are mostly made near the melting point; however, it is the lower temperature properties that mainly concern adhesive studies. Therefore, surface energies of solids are generally indirectly estimated through contact angle measurement methods.

In a contact angle measurement, a drop of liquid is placed upon the surface of a solid. It is assumed that the liquid does not react with the solid and that the solid surface is perfectly smooth and rigid. The drop is allowed to flow and equilibrate with the surface. The measurement of the contact angle,  $\theta$  (theta), is usually made with a goniometer that is simply a protractor mounted inside a telescope. The angle that the drop makes with the surface is measured carefully. A diagram of the contact angle measurement is shown in Figure 1.

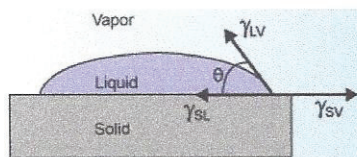


Figure 1: Schematic diagram of the contact angle and its surface free energy (tension) components

A rather simple method of estimating the surface energy of solids was developed by Zisman<sup>2</sup>. Zisman proposed that a critical surface tension,  $\gamma_c$ , can be estimated by measuring the contact angle of a series of liquids with known surface tensions on the surface of interest. These contact angles are plotted as a function of the  $\gamma_{LV}$  of the test liquid. The critical surface tension is defined as the intercept of the horizontal line,  $\cos \theta = 1$ , with the extrapolated straight-line plot of  $\cos \theta$  against  $\gamma_{LV}$  as shown in Figure 2. This intersection is the point where the contact angle is 0 degrees. A hypothetical test liquid having this  $\gamma_{LV}$  would just spread over the substrate.

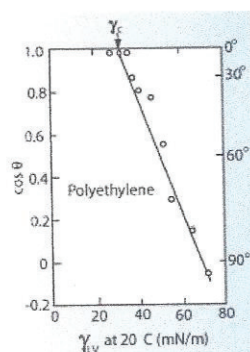


Figure 2: Zisman plot for low energy polyethylene surface with a liquid series commonly used by Zisman<sup>3</sup>

The surface tension value for most inorganic solids is on the order of hundreds or thousands of mJ/m<sup>2</sup>, and for polymers it is at least an order of magnitude lower. Solid substrates are often considered to be either "high energy surfaces" (metals, glass, ceramics) or "low energy surfaces" (polymers). Organic liquids have surface tensions that are in a similar range as solid polymers. In fact, an epoxy adhesive composition will have approximately the same surface tension in the cured state as it does in the uncured or liquid state. Values of critical surface tensions for common solids and surface tensions of common liquids are shown in Table 1.

Liquids	Surface Tension, dynes/cm
Epoxy resin (DGEBA type)	47
Petroleum lubricating oil	29
Silicone oil	19
Glycerol	64
Hexane	18
Acetone	23
n-Propanol	24
Toluene	28
Trichloroethane	25
Methyl ethyl ketone	25
Ethylene glycol	48
Mineral spirits	24
Water	73

Substrates (High Energy) Critical Surface Tension, dynes/cm	
Aluminum	~500
Copper	1360
Nickel	1770
Iron oxide	1357
Beryllium oxide	1360
Lead	442
Silver	890
Glass	~1000

Substrates (Low Energy)	Critical Surface Tension, dynes/cm
Acetal	47
Acrylonitrile butadiene styrene - ABS	35
Acrylic	41
Epoxy - typical amine cure	46
Nylon 6/6	41
Polycarbonate	46
Polyethylene terephthalate - PET	43
Polyimide	40
Polystyrene	33
Polysulfone	41
Polytetrafluoroethylene - PTFE	18
Polyvinyl chloride - PVC	39
Polyethylene	31
Polypropylene	33
Phenolic	52
Silicone	24
Styrene butadiene rubber	29

Table 1: Room Temperature Surface Tension of Several Liquids (Top) and Critical Surface Tension of Various High Energy (Middle) and Low Energy Substrates (Bottom)

References

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3. Kinloch, A.J., Adhesion and Adhesives, Chapman and Hall, New York, 1987, p. 25.

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[Edward M. Petrie](#)

Declaration of Robert A. Iezzi, Ph.D.  
APPENDIX N-2

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SpecialChem4Adhesives Members Reactions

**USING OTHER TOOLING THAN Goniometer** - May 06, 2011

posted by Jose Castellanos, Analytical laboratory / Testing at Converteam

I am going to study a new braze material. I want to use other tooling than a Goniometer to make easier and more accurate contact angle measurement. I let you know later if my hypothesis was the right one. Note: I have measure superficial and interfacial tension on liquids since 1990.

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**fascinating and very useful** - Apr 29, 2011

posted by Steve Strunk, Production / Manufacturing at Teledyne Dalsa

Great article. Instructive and very practical method to measure surface energy/tension.

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