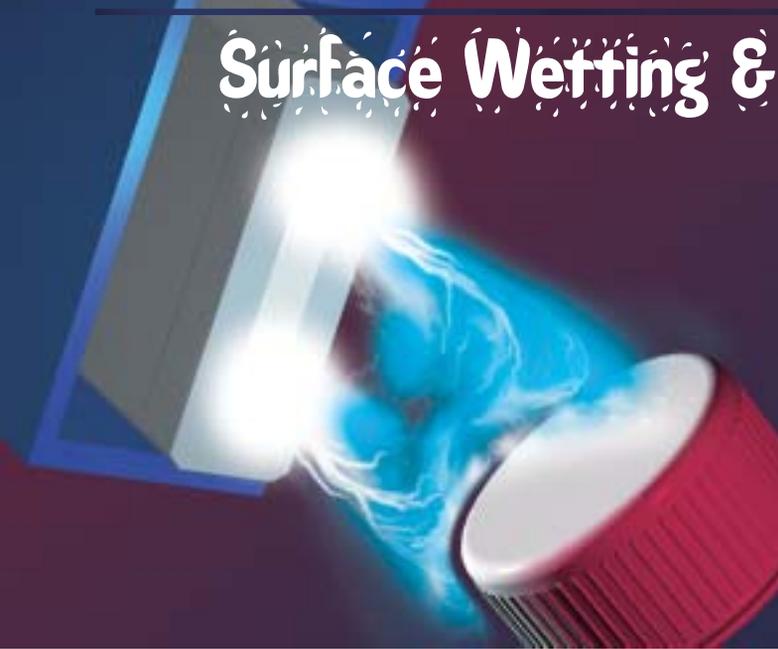


Surface Wetting & Pretreatment Methods

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Surface Energies of Untreated Polymers

Hydrocarbons	Surface energy (dynes/cm)
Polypropylene, OPP, BOPP	29-31
Polyethylene	30-31
Polyvinyl Acetate (PVA) Copolymer	33-44
Polystyrene	38
Polystyrene (low ionomer)	33
ABS	35-42
Polyamide	<36
Epoxy	<36
Polyester	41-44
Rigid PVC	39
Plasticized PVC	33-38

Engineering Thermoplastics

PET	41-44
Polycarbonate	46
Polyimide	40
Polyacetal	<36
Polyphenylene oxide (PPO)	47
PBT	32
Polysulfone	41
Polyethersulfone	50
Polyphenylene sulfide (PPS)	38
Nylon	33-46

Fluorocarbons

Polyethylene copolymer	20-24
Fluorinated ethylene propylene	18-22
Polyvinyl fluoride	28

Elastomers

Silicone	24
Natural rubber	24
Styrene butadiene rubber	48

Figure 2

Pretreatment Procedures

The degree or quality of treatment is affected by the cleanliness of the plastic surface. The surface must be clean to achieve optimal pretreatment and subsequent adhesion. Surface contamination such as silicone mold release, dirt, dust, grease, oils, and fingerprints inhibit treatment. Material purity is also an important factor. The shelf life of treated plastics depends on the type of resin, formulation, and the ambient environment of the storage area. Shelf life of treated products is limited by the presence of low molecular weight oxidized materials (LMWOM) such as antioxidants, plasticizers, slip and antistatic agents, colorants and pigments, and stabilizers, etc. Exposure of treated surfaces to elevated temperatures increases molecular chain mobility - the higher the chain mobility the faster the aging of the treatment. Polymer chain mobility in treated materials causes the bonding sites created by the treatment to move away from the surface. These components

Plastics adhesion problems are widespread throughout the industry. A major contributing factor to these problems is that many plastics have chemically inert and nonporous surfaces with low surface tensions. That is, most plastics are hydrophobic and are not naturally wettable. These properties, although advantageous to the design engineer, often result in secondary assembly and decorating concerns in the areas of bonding, printing, coating and painting. However, surface pretreatments on today's high performance engineering resins will solve many adhesion problems while increasing bond strength performance.

As a general rule, acceptable bonding adhesion is achieved when the surface energy of a substrate (measured in dynes/cm) is approximately 10 dynes/cm greater than the surface tension of the liquid. In this situation, the liquid is said to "wet out" or adhere to the surface. Surface tension, which is a measurement of surface energy, is the property (due to molecular forces) by which all liquids through contraction of the surface tend to bring the contained volume onto a shape having the least surface area. Therefore, the higher the surface energy of the solid substrate relative to the surface tension of a liquid, the better will be its "wettability", and the smaller the contact angle (Figure 1).

As many plastics are hydrophobic and are not naturally "wetable", the table in Figure 2 lists typical surface energies for untreated polymer substrates. Due to the vast differences between resin formulations, the values listed below should be used for general benchmark purposes.

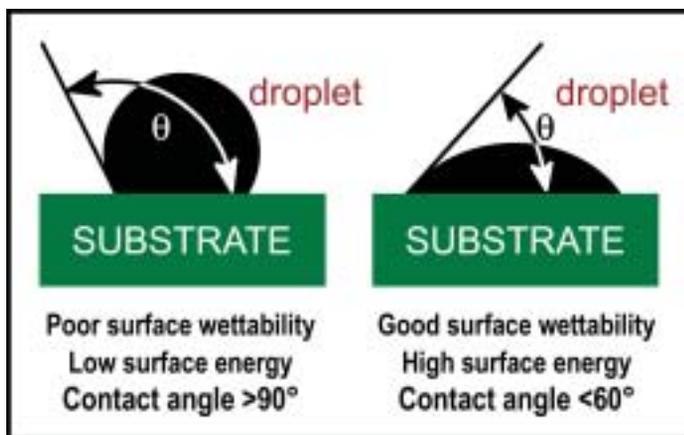


Figure 1

may eventually migrate to the polymer surface. Therefore, it is recommended to bond, coat, paint, or decorate the product as soon as possible after pretreatment.

Surface pretreatments are used to increase surface energy and improve the wetting and adhesive properties of polymer materials. A variety of gas-phase surface oxidation pretreatment processes are used in the industry including low pressure cold gas plasma (Microwave/RF), electrical (corona discharge), and flame plasma. Each method is application-specific and possesses unique advantages and potential limitations (Figure 3). All of these processes are characterized by their ability to generate a “gas plasma” – an extremely reactive gas consisting of free electrons, positive ions, and other chemical species. In the science of physics, the mechanisms in which these plasmas are generated are different but their effects on surface wettability are similar. Plasmas can be conceptualized as a fourth state of matter. If sufficient energy is supplied, solids melt into liquids, liquids vaporize into gases, and gases ionize into plasmas.

Free electrons, ions, metastables, radicals, and UV generated in plasma regions can impact a surface with energies sufficient to break the molecular bonds on the surface of most substrates. This creates very reactive free radicals, on the polymer surface which in turn can form, cross-link, or in the presence of oxygen, react rapidly to form various chemical functional groups on the substrate surface. Polar functional groups that can form and enhance bondability include carbonyl (C=O), carboxyl (HOOC), hydroperoxide (HOO-), and hydroxyl (HO-) groups. Even small amounts of reactive functional groups incorporated into polymers can be highly beneficial to improving surface characteristics and wettability.

The global need to achieve robust adhesive bonding on plastics demands state-of-the-art surface pretreatment systems capable of achieving high volume production under a broad range of manufacturing applications. Several pretreatment options exist. Each project application is unique. The degree (effectiveness) of treatment on a surface is affected by prior operations such as molding and parts handling. Pretreated oxidized surfaces can affect downstream assembly process. Successful implementation (Six Sigma) is dependent upon careful evaluation of all process factors and thorough understanding of each pretreatment method. ■

Scott R. Sabreen is Founder & President of The Sabreen Group (TSG). TSG is an engineering company specializing in Secondary Plastics Manufacturing Operations — surface pretreatments, bonding, decorating & finishing and laser marking. For more information call toll-free at 888-SABREEN or visit: www.sabreen.com.

Surface Wetting Test Procedure Using Dyne Solutions

This procedure describes a method for testing and measuring the surface wetting tension, i.e., surface energy, of plastic substrates using dyne test marker pens.

Surface wetting tests should be conducted immediately after pretreatment (corona discharge, flame treatment, RF gas plasma). Treated surfaces are time sensitive and are affected by environmental conditions such as temperature and humidity. Substrates must have clean surfaces for optimal adhesion. Dirt, dust, hand/finger oils, silicone based products, and other contaminants inhibit adhesion and can cause erroneous test results.

CAUTION: Dyne solutions contain Cellosolve (2-ethoxyethanol) and Formamide which are considered hazardous chemicals. Avoid contact with skin and eyes. Gloves must be worn at all times. Use with adequate ventilation. Pregnant women should not perform this test. Refer to MSDS sheet supplied by the vendor.

1.0 MATERIALS/EQUIPMENT

- 1.1 Dyne marker pens — levels available
30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 60
- 1.2 Products to be tested
- 1.3 Plastic gloves
- 1.4 Chemwipes or paper towels
- 1.5 Temperature and humidity gages
- 1.6 Clean work area

Note: Dyne solutions typically have a 6-12 month shelf life. Products should be immediately disposed when the solutions appear green in color. Store in a cool dark area.

2.0 METHOD

- 2.1 Record ambient temperature and humidity
- 2.2 Select 60 dyne pen, and remove the cap
- 2.3 Place the product to be tested on a flat surface.
Firmly press the marker pen applicator tip down onto the product until solution is drawn into the tip.
- 2.4 Using a light touch, draw the pen across the length of the pretreated surface one time to apply a thin fluid layer.
2-3 parallel passes are recommended.
Excessive solution will result in misreading
- 2.5 Note the time it takes for the liquid to break into droplets.
The reading of the liquid behavior should be observed in the center of the liquid
- 2.6 If the liquid does not break into droplets after two (2) seconds, then the surface energy is assumed to be a minimum of 60 dynes. Proceed to step 2.7. If the liquid breaks into droplets in less than two (2) seconds, repeat the test using the next lower dyne marker pen.
Adjustments to the pretreatment process may be necessary
- 2.7 The test is completed when all surfaces achieve the desired wetting results
- 2.8 Properly discard tested products

Note: Never retest the same location on a sample. Do not touch or contaminate the surface to be tested. Dyne solutions are also available in bottle containers, and may be used in conjunction with a cotton swab test (ASTM D2578-84).

	Applications	Advantages	Limitations
Cold Gas Plasma	active microcircuits, thin films, plasma enhanced chemical vapor deposition (PECVD)	cleans substrate surfaces, relatively long shelf life, surface grafting	high equipment cost, normally conducted off-line batch process
Corona discharge	non-active electronic components, bottles, containers, pens, automotive parts	in-line treatment, irregular shaped parts, process control, relatively low cost	humidity changes can affect treatment level, does not clean parts, avoid parts with metal inserts
Flame Plasma	bottles, containers, pens	in-line treatment, low cost, removes flash	heat can affect surface appearance, open flame, process set-up is more difficult to control

Figure 3