

Standard Test Method for Corona-Treated Polymer Films Using Water Contact Angle Measurements¹

This standard is issued under the fixed designation D 5946; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers measurement of the contact angle of water droplets on corona-treated polymer film surfaces.

NOTE 1—There is no similar or equivalent ISO standard.

1.2 The values stated in SI units are to be regarded as the standard. The values given in brackets are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D 618 Practice for Conditioning Plastics for Testing

D 724 Test Method for Surface Wettability of Paper (Angle-of-Contact Method)

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *static contact angle, θ (degrees), n*—the angle between the substrate surface and the tangent line drawn to the droplet surface at the three-phase point, when a liquid drop is resting on a plane solid surface.

3.1.1.1 *Discussion*—Contact angle values can be determined as follows: (1) by analyzing an image of a droplet using various projection or reflective devices and measuring the contact angle directly with a protractor by using tangential alignment of a cursor line or the use of reference alignment procedures (Test Method D 724); or (2) by analyzing an image

of a droplet using various projection or reflective devices and measuring the height and width on the substrate surface to calculate the contact angle as follows:

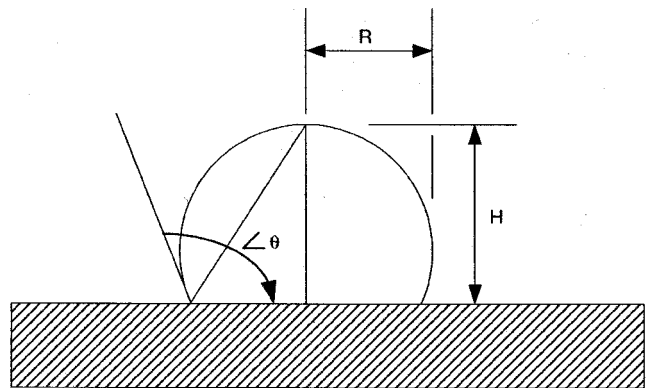
$$\theta = 2 \cdot \arctan (H/R) \quad (1)$$

where:

θ = contact angle,

H = height of a droplet's image, and

R = half its width.



3.1.1.2 *Discussion*—Instrumentation is also available that utilizes an image and directly determines the contact angle based on the calculation shown for Method (2) of U.S. Patent No. 5,268,733.

3.1.1.3 *Discussion*—Method (1) may be biased due to the subjective nature of visually finding a tangent to the droplet image at the three-phase point; if Method (1) is to be used, the bias of each operator's measurements shall be determined. Because Method (2) utilizes measured dimensions of the droplet, it would be expected to have less bias. Comparative analyses using these various procedures have not been conducted. Therefore, caution is recommended when comparing data obtained from these different methods.

3.1.1.4 *Discussion*—Method (2) may not be applicable in special cases in which the contact angle is greater than 90°

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

4. Summary of Test Method

4.1 In this test method, drops of water are placed on the surface of a film sample, and the contact angle values are measured and then averaged.

5. Significance and Use

5.1 The ability of polymer films to retain inks, coatings, adhesives, etc. is primarily dependent on the character of their surfaces and can be improved by one of several surface-treating techniques. The electrical discharge treatment, such as corona treatment, has been found to increase the wetting tension of a polymer film. The stronger the treatment, the more actively the surface reacts with different polar interfaces. It is therefore possible to relate the contact angle of a polymer film surface to its ability to accept and retain inks, coatings, adhesives, etc., if the ink, coating, or adhesive contains the polar functionalities. Contact angle in itself is not a completely acceptable measure of ink, coating, or adhesive adhesion.

5.2 The wetting tension of a polymer film belongs to a group of physical parameters for which no standard of accuracy exists. The wetting tension of a polymer cannot be measured directly because solids do not change shape measurably in reaction to surface energy. Many indirect methods have been proposed.³ Different test methods tend to produce different results on identical samples. Practical determination of a solid's surface energy uses this interaction of the solid with test liquids.

5.3 Although the level of surface treatment of polymer films has been traditionally defined in the industry in terms of dynes/cm (mN/m), these values are derived from a subjective interpretation of the observed test liquid behavior.

5.4 The following ranges of water contact angle values can be used as a guide for defining the level of surface treatment of polyolefins and many other polymer films with initial low surface energies:

| | |
|--------------------------|-----------|
| Marginal or no treatment | >90° |
| Low treatment | 85 to 90° |
| Medium treatment | 78 to 84° |
| High treatment | 71 to 77° |
| Very high treatment | <71° |

5.4.1 The suitability of the test for specification acceptance, manufacturing control, and end use of polymer films will have to be established through capability studies for each particular film and treatment.

5.5 Almost all materials have variations in contact angle as one moves from point to point. Nonuniform treatment of film with corona treaters may also add variability to the results. Therefore, multiple measurements are necessary to reflect variation in treatment and surface roughness.

6. Interferences

6.1 The wetting tension of a polymer film in contact with a drop of liquid in the presence of air is a function of the surface energies of both the air-film and film-liquid interfaces; any trace of surface-active impurities in the test liquid or on the

film may affect the results. It is therefore important that the portion of the film surface to be tested not be touched or rubbed, that all equipment be scrupulously clean, and that water purity be guarded carefully. Glass apparatus, in particular, is likely to be contaminated with detergents having very low surface tension, unless specific precautions are taken to ensure their absence, such as cleaning with chromic sulfuric acid and rinsing with distilled water.

6.2 The presence of slip, antistatic, or antiblocking and other additives can change the surface of the film since these additives leach out to the surface with time.

6.3 Finely embossed films add more variability to the measurements.

6.4 Polymer films often generate static charges when they are processed. Corona treatment usually exacerbates the problems. The film sample for surface measurement may carry the static charge generated in processing or may acquire a charge by friction when sliding over the specimen holder surface.

6.4.1 The static charges may cause errors in contact angle measurements. These errors occur as the electrostatic field generated by the charged sample pulls the water droplet to the film surface stronger than it would be in the absence of charges.

6.4.2 To prevent measurement errors, the film sample shall be kept free of static buildup before and during measurements by placing an air ionizer, also known as a static eliminator, in the vicinity of the specimen holder. These devices produce air ions of positive and negative polarity. The charged object in the vicinity of the ionizer will attract ions of the opposite polarity and will be neutralized.

6.5 The transfer of a droplet onto the measured surface shall be accomplished following the procedure described in Section 11. An improper transfer technique increases the variability of measurements.

6.6 The contact angle measuring method using tangential alignment of the cursor line of a protractor, as described in 3.1.1.1 (1), is biased due to the subjective nature of finding a tangent to the droplet image at the three-phase point. The smaller the measured contact angle, the larger the error. The bias of each operator's measurements shall be determined if this method is to be used.

7. Apparatus

7.1 *Contact Angle Meter, or Goniometer*—The apparatus for measuring contact angles shall contain the following: (1) a liquid dispenser capable of suspending a precise droplet of the specified volume from the tip of the dispenser, (2) a sample holder that can stretch a film sample flat without wrinkles and distortions, (3) provisions for bringing the sample toward the suspended droplet in a controlled manner to accomplish droplet transfer onto the measured surface, and (4) means for projecting a "silhouette" image of the drop with minimal distortions. The apparatus shall have means for direct angle measurements, such as a protractor, or direct measurements of the droplet's dimensions, such as a grid or scale, or both, or a suitable charge coupled device sensor and analysis hardware and software appropriate for subsequent analysis.

³ Wu, S., *Polymer Interface and Adhesion*, Marcel Dekker, Inc., New York, NY, 1982.

8. Reagents and Materials

8.1 *Purity of Water*—Deionized ultra filtered water should be used for testing purposes. The test liquid shall be kept in scrupulously clean containers.

9. Sampling

9.1 The minimum amount of film required for this test is an approximately 25-mm wide and 300-mm long sample strip. If a sample is taken from a roll, the direction of the sample relative to the machine direction of the web shall be noted.

9.2 Extreme care shall be taken to prevent the surface of the film sample from being touched or handled in the areas upon which the test is to be made.

9.3 The number of measurements per film sample can be determined using published tables for sampling plans. Complete tables can be found in most books on quality control.⁴ The recommended number of readings per sample is ten.

9.4 For the purpose of determining the contact angle profile across the width of the roll, one contact angle measurement can be taken every 25 mm [1 in.] across the sample.

10. Conditioning

10.1 Conditioning is not generally required for routine quality assurance (QA) or process control measurements since conditioning may affect the measured value and misrepresent the actual conditions.

10.2 Conditioning is required for interlaboratory measurements intended to compare the results. Condition the test specimens at $23 \pm 2^\circ\text{C}$ [$73.4 \pm 3.6^\circ\text{F}$] and $50 \pm 5\%$ relative humidity for not less than 40 h prior to testing in accordance with Procedure A of Practice D 618, for those tests in which conditioning is required. In cases of disagreement, the tolerances shall be $\pm 1^\circ\text{C}$ [$\pm 1.8^\circ\text{F}$] and $\pm 2\%$ relative humidity.

10.3 *Test Conditions*—Special test conditions are not generally required for routine QA or process control measurements.

10.4 *Test Conditions for Interlaboratory Studies*—Whenever possible, conduct tests in the standard laboratory atmosphere of $23 \pm 2^\circ\text{C}$ [$73.4 \pm 3.6^\circ\text{F}$] and $50 \pm 5\%$ relative humidity, unless otherwise specified in the test methods or in this test method. In cases of disagreement, the tolerances shall be $\pm 1^\circ\text{C}$ [$\pm 1.8^\circ\text{F}$] and $\pm 2\%$ relative humidity.

11. Procedure

11.1 Place a sample strip onto the specimen holder of the instrument. Make sure the film sample is lying flat without wrinkles and distortions.

11.2 Suspend a 5 to 8- μL droplet at the end of a syringe needle. Bring the surface with the mounted sample upward until it touches the pendant drop. Then lower the surface with the sample to complete the droplet transfer. Do not drop or squirt droplets on the surface. See Fig. 1.

11.3 Follow the instrument manufacturer’s instructions for a maximum time between dropping of the water droplet and measurement. Use the measurement techniques listed in 3.1.1.1.

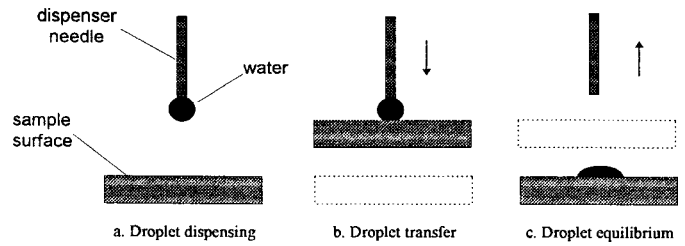


FIG. 1 Water Droplet Transfer Technique

11.4 Advance the sample to place the next droplet onto a previously untouched area.

11.5 Take ten contact angle measurements on the sample.

12. Calculation

12.1 *Calculation:*

12.1.1 Calculate the average of the ten measurements.

12.1.2 Calculate the standard deviation of the measurements.

12.1.3 *Example:*

- | | |
|---------|----------|
| (1) 66° | (6) 72° |
| (2) 72° | (7) 72° |
| (3) 66° | (8) 72° |
| (4) 72° | (9) 69° |
| (5) 73° | (10) 69° |

Average contact angle: 70°. This result corresponds to the lower end of the very high treatment level. Standard deviation: 2.4°.

13. Report

13.1 Report the instrument used, number of readings, average value of the contact angle measurements and standard deviation, method used for determination of contact angle, temperature, humidity, and any comments and observations.

14. Precision and Bias

14.1 *Precision:*

14.1.1 Instrument error depends on the instrument used. The instrument error can be assessed by measuring a uniform surface such as solidified paraffin wax and calculating the standard deviation of the measurements.

14.1.2 *Precision of the Test*—Table 1 is based on an interlaboratory study conducted in 1995 in accordance with Practice E 691 involving four materials and eight laboratories. Each test result was the average of ten individual determinations. Each laboratory obtained three test results for each material on two days. The results demonstrate that the precision of the results is generally independent of the treatment level (wetting tension) of the film. (**Warning**—The following explanations of *r* and *R* are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be applied rigorously to the acceptance or rejection of material, as those data are specific to the interlaboratory study and may not be representative of other lots, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their

⁴ Duncan, J. A., *Quality Control and Industrial Statistics*, 3d Ed., Irwin, Homewood, IL, 1965.

TABLE 1 Interlaboratory Study Results

| Material | Treatment Power, W/ft ² /min | Average Contact Angle, ° | Repeatability Standard Deviation, S_r | Reproducibility Standard Deviation, S_R | r | R |
|----------------------------|---|--------------------------|---|---|------|-------|
| HDPE film with EVA backing | 10 | 68.99 | 1.60844 | 2.84039 | 4.50 | 7.95 |
| HDPE film with EVA backing | 2 | 69.39 | 2.41652 | 3.11040 | 6.77 | 8.71 |
| HDPE film with EVA backing | 1 | 75.03 | 2.15706 | 3.08072 | 6.04 | 8.63 |
| Polypropylene film | pre-treated | 85.00 | 1.95980 | 4.03218 | 5.49 | 11.29 |

laboratory and materials, or between specific laboratories. The principles of 14.1.3-14.2 would then be valid for such data.)

14.1.3 *Concept of r and R* —If S_r and S_R have been calculated from a large enough body of data, and for test results that were averages of ten test determinations:

14.1.3.1 *Repeatability, r (Single Operator)*—The two test results should be judged not equivalent if they differ by more than the r contact angle degrees for that treatment level.

14.1.3.2 *Reproducibility, R (Multilaboratory)*—The two test results should be judged not equivalent if they differ by more than the R contact angle degrees for that treatment level.

14.1.3.3 Any judgment per 14.1.3.1 and 14.1.3.2 would have an approximate 95 % (0.95) probability of being correct.

14.2 *Bias*—No statement can be made regarding the bias of this test method because the contact angle is defined in terms of the test method.

15. Keywords

15.1 contact angle; contact angle meter; corona treatment; goniometer; polymer films; surface treatment; water

APPENDIXES

(Nonmandatory Information)

X1. ADDITIONAL INFORMATION

X1.1 There exists a relationship between the contact angle between a polymer film and water and the surface energy of the film. It is also documented that different materials, other measuring techniques, and different surface textures will produce variation in the relationship between contact angle and surface energy. However, these appendixes are presented to provide insight into one set of relationships found for a typical film treated at a large number of energy levels.

X1.2 When a drop of liquid rests on the surface of a solid, and a gas is in contact with both, the forces acting at the interfaces must balance. These forces can be represented by various surface tensions acting in the direction of the surfaces, and it follows that

$$\gamma_{GL} \cos \theta = \gamma_{GS} - \gamma_{SL} \quad (X1.1)$$

where:

θ = angle of contact of the edge of the drop with the solid surface,

γ_{GL} = surface tension of the gas-liquid interface,

γ_{GS} = surface tension of the gas-solid interface, and

γ_{SL} = surface tension of the solid-liquid interface.

When the air is saturated with vapors of the liquid, γ_{GL} will be the surface tension of the liquid.

X1.3 This appendix reports a unique condition in which films treated to different levels can be considered a homologous polymer series. For such a series, the relationship between the $\cos \theta$ of water droplets and wetting tension, γ_c , was found to be linear:⁵

$$\gamma_c = k_1 \gamma_{GL} - (1 - \cos \theta)/k_2 \quad (X1.2)$$

where the parameters k_1 and k_2 are constants.

X1.3.1 In this form, the relationship can be used to estimate the wetting tension of corona-treated surfaces from the water contact angle data. In this case, the value γ_{GL} is fixed at 72 mN/m for water, while the contact angle and its cosine will be changing depending on the surface energy of the substrate.

X1.3.2 Since the wetting tension of a polymer film belongs to a group of physical parameters for which no standard of accuracy exists, a range of values for wetting tension corresponding to a given water contact angle value is used to correlate the contact angle data to the wetting tension. The values of k_1 and k_2 range from 0.75 to 0.9 for k_1 and from 0.35 to 0.46 for k_2 . A conversion chart is given in Appendix X2.

⁵ Blitshteyn, M., "Wetting Tension Measurements on Corona-Treated Polymer Films," *TAPPI Journal*, Vol 78, No. 3, March 1995, pp. 138-143.

X2. WATER CONTACT ANGLE TEST FOR WETTING TENSION (WCAT)
TABLE X2.1 Conversion Chart

| Water contact angle, ° | Dyne test approximation, dyne/cm |
|------------------------|----------------------------------|
| 51 | 46 |
| 52 | 46 |
| 53 | 46 |
| 54 | 45 |
| 55 | 45 |
| 56 | 45 |
| 57 | 44 |
| 58 | 44 |
| 59 | 44 |
| 60 | 43 |
| 61 | 43 |
| 62 | 43 |
| 63 | 42 |
| 64 | 42 |
| 65 | 42 |
| 66 | 41 |
| 67 | 41 |
| 68 | 41 |
| 69 | 40 |
| 70 | 40 |
| 71 | 40 |
| 72 | 39 |
| 73 | 39 |
| 74 | 38 |
| 75 | 38 |
| 76 | 38 |
| 77 | 37 |
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| 79 | 37 |
| 80 | 36 |
| 81 | 36 |
| 82 | 35 |
| 83 | 35 |
| 84 | 35 |
| 85 | 34 |
| 86 | 34 |
| 87 | 34 |
| 88 | 33 |
| 89 | 33 |
| 90 | 32 |
| 91 | 32 |
| 92 | 32 |
| 93 | 31 |
| 94 | 31 |
| 95 | 31 |
| 96 | 30 |
| 97 | 30 |
| 98 | 29 |
| 99 | 29 |
| 100 | 29 |

SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D20 has highlighted those changes that impact the use of this test method. This section includes descriptions of the changes or the reasons for the changes, or both.

D 5946-04:

(1) Revised the contact angle figure found in 3.1.1.1.

D 5946-01:

(1) Revised Discussions to 3.1.1 to clarify and correct description of methods.

D 5946-99:

(1) In 1.1, deleted phrase.

(2) In 3.1.1, deleted definitions of *polarity*, *surface energy*, *surface tension*, and *wetting tension*.

(3) In 5.1, deleted polarity and wetting tension.

(4) In Section 5, deleted discussion of the relationship between contact angle, surface energy, and wetting tension (formerly 5.4 and 5.5).

(5) In 5.4, deleted approximate surface energies.

(6) In 5.5, incorporated surface energy and surface roughness.

(7) Changed 6.4 for readability.

(8) In 7.1, updated video camera language to reflect current terminology/technology.

(9) In 9.4, replaced wetting tension and inserted proper SI units.

(10) Retitled Section 12 and deleted 12.2 and 12.3.

(11) In 13.1, deleted reference to conversion table.

(12) In 15, removed wetting tension.

(13) X1.1 added as explanatory paragraph.

(14) In X1.2, removed text reference to deleted 5.4.

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