Designation: D5946 – 17

Standard Test Method for
Corona-Treated Polymer Films Using Water Contact Angle Measurements[1]

1. Scope*

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

NOTE 1—This standard is identical to ISO 15989.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses 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.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D618 Practice for Conditioning Plastics for Testing

D724 Test Method for Surface Wettability of Paper (Angle-of-Contact Method) (Withdrawn 2009)[3]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *ISO Standard:*[4]

ISO 15989 Plastics—Film and Sheeting—Measurement of Water-Contact Angle of Corona-Treated Films

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 D724); 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:

$$\theta = 2 \cdot \arctan(H/R) \qquad (1)$$
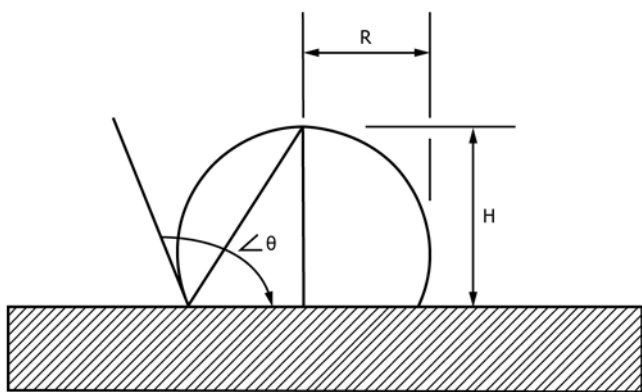
where:
θ = contact angle,
H = height of a droplet's image, and
R = half its width.

---

*A Summary of Changes section appears at the end of this standard

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°

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.[5] Different test methods tend to produce differ-ent 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 will potentially effect 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 carefully controlled. 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, antiblocking, or other additives has the potential to change the surface of the film.

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 prob-lems. The film sample for surface measurement has the potential to 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 have the potential to cause errors in contact angle measurements. These errors occur as the electro-static 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

---

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

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*) if equipped, with a sample holder it needs to stretch the film to provide a flat surface without wrinkles and distortions, if unit does not have a sample holder, care needs to be taken to provide a flat surface without wrinkles and distortions, (*3*) provisions for bringing the sample in contact with the 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.

8. Reagents and Materials

8.1 *Purity of Water*—It is suggested to use 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 recommended number of readings per sample is ten.

NOTE 2—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.[6]

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.

---

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

10. Conditioning

10.1 Conditioning is not generally required for routine quality assurance (QA) or process control measurements. Conditioning will potentially 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 $23 \pm 2°C$ ($73.4 \pm 3.6°F$) and 50 ± 10 % relative humidity for not less than 40 h prior to testing in accordance with Procedure A of Practice D618 unless otherwise specified by agreement or the relevant ASTM material specification. In cases of disagreement, the tolerances shall be $\pm1°C$ ($\pm1.8°F$) and ±5 % 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*—Conduct tests in the standard laboratory atmosphere of $23 \pm 2°C$ ($73.4 \pm 3.6°F$) and 50 ± 10 % relative humidity, unless otherwise specified by agreement or the relevant ASTM material specification. In cases of disagreement, the tolerances shall be $\pm1°C$ ($\pm1.8°F$) and ±5 % 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. Alternatively, the syringe may be lowered to the specimen to release the droplet.

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.

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:*
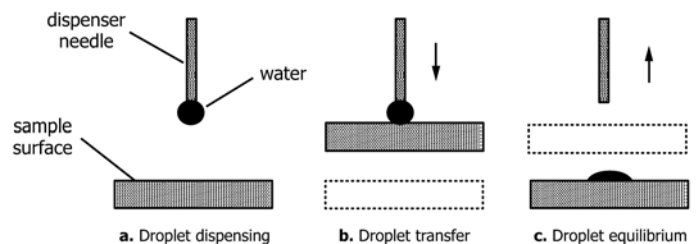12.1.1 Calculate the average of the ten measurements.

FIG. 1 Water Droplet Transfer Technique

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 following information:

13.1.1 Instrument used.

13.1.2 Number of readings.

13.1.3 Average value of the contact angle measurement and standard deviation.

13.1.4 Method used for determination of contact angle.

13.1.5 Temperature, humidity, and any comments and observations.

14. Precision and Bias

14.1 *Precision:*

14.1.1 Instrument error depends on the instrument used. An example of assessing instrument error is to measure a uniform surface such as solidified paraffin wax and then calculate 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 E691 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 explanation 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 to the acceptance or rejection of materials, as those data apply only to the materials tested in the round robin and are unlikely to be rigorously representative of other lots, formulations, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E691 to generate data specific to their 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*—Two results obtained within one laboratory shall be judged not equivalent if they differ by more than the *r* value for that material. *r* is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

14.1.3.2 *Reproducibility*—Two test results obtained by different laboratories shall be judged not equivalent if they differ by more than the *R* value for that material. *R* is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories

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*—There are no recognized standards by which to estimate bias of this method.

15. Keywords

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

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

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

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

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 θ of water droplets and wetting tension, γ_c, was found to be linear:[7]

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

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.

---

[7] 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
78	37
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

Committee D20 has identified the location of selected changes to this standard since the last issue (D5946 - 09) that may impact the use of this standard. (May 1, 2017)

(1) Updated 7.1 to account for units that do not have a sample holder and added provision for units that lower the syringe to the sample.

(2) Updated 11.2 to account for units that lower the syringe to the sample surface.

(3) Revised ISO equivalency statement to align with ASTM D4968 the standard guide to review.

(4) Revised Section 6 (6.1, 6.2, 6.4, 6.4.1) to remove the use of permissive language.

(5) Revised 7.1 as a permissive language edit.

(6) Revised 8.1 as a permissive language edit.

(7) Revised 9.3 as a permissive language edit and sentence one has become Note 2.

(8) Revised 10.1 as a permissive language edit.

(9) Revised 14.1.1 as a permissive language edit.

(10) Edited 14.1.2, 14.1.3.1, 14.1.3.2, and 14.2 to reflect language in D4968, the standard guide to review.