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Plastics — Film and sheeting — Measurement of water-contact angle of corona-treated films

Plastiques — Film et feuille — Détermination de l'angle de contact avec l'eau des feuils traités par effluve

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15989 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 11, *Products*.

Plastics — Film and sheeting — Measurement of water-contact angle of corona-treated films

1 Scope

This International Standard specifies a method of measuring the contact angle of water droplets on corona-treated polymer film surfaces and subsequently determining the wetting tension of the film.

The method is applicable to practically any polymer film. It is not applicable, however, if the surface of the film exhibits a chemical affinity for water.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ASTM E 691:1999, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* (Equivalent to ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*)

ASTM D 724, *Standard Test Method for Surface Wettability of Paper (Angle-of-Contact Method)*

ASTM D 5946, *Standard Test Method for Corona-Treated Polymer Films Using Water Contact Angle Measurements*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

surface energy

energy associated with the intermolecular forces at the interface between two surfaces, measured as free energy per unit area

NOTE It is expressed in mN/m.

3.2

wetting tension

γ_c

tension taken to be equal to the surface tension of the liquid which just exhibits a zero contact angle with the surface of a polymer film

NOTE This is used to give an estimate of the film's surface energy in mN/m. The unit dyne/cm is also used in industry for surface energy and wetting tension (1 dyne/cm = 1 mN/m).

3.3
polarity
value which quantifies the concentration of polar functional groups on a polymer film surface

NOTE It is expressed as the polar component of the surface energy over the total surface energy.

3.4
static contact angle
θ
angle between a plane solid surface and the tangent drawn in the vertical plane at the interface between the plane solid surface and the surface of a droplet of liquid resting on the surface

4 Principle

Droplets of water are placed on a specimen of film and the contact angle measured. The wetting tension of the film is then determined from a conversion chart.

See Annex A for the significance and use of contact-angle measurements and Annex B for interference effects in the measurement of the contact angle.

5 Apparatus

5.1 Contact-angle meter (goniometer)

A commercially available contact-angle meter, including a light source, optical system, specimen stage and liquid delivery system, may be used.

The light source can be a halogen, incandescent or fibre-optic type of lamp, as long as neither the specimen nor the liquid is affected by the heat from the light source.

The viewing optics can be video, CCD camera, ocular lens or projection optics and shall be configured such that magnifications from $\times 6$ to $\times 30$ can be used.

The specimen stage shall be such that the specimen can be positioned with the test surface flat and horizontal. When the specimen is moved to view a new area, it shall be possible to avoid the previously wetted area.

The liquid-delivery system shall be a pump-driven or manual microsyringe. For the greatest droplet-formation accuracy, a small-capacity, i.e. 100 µl to 250 µl, microsyringe shall be used.

In order to be able to test liquids requiring different droplet sizes, it shall be possible to accommodate flat-tipped needles of various gauges from 24 gauge to 32 gauge. Stainless-steel needles are preferred, but other types, such as needles coated with polytetrafluoroethylene, may also be used.

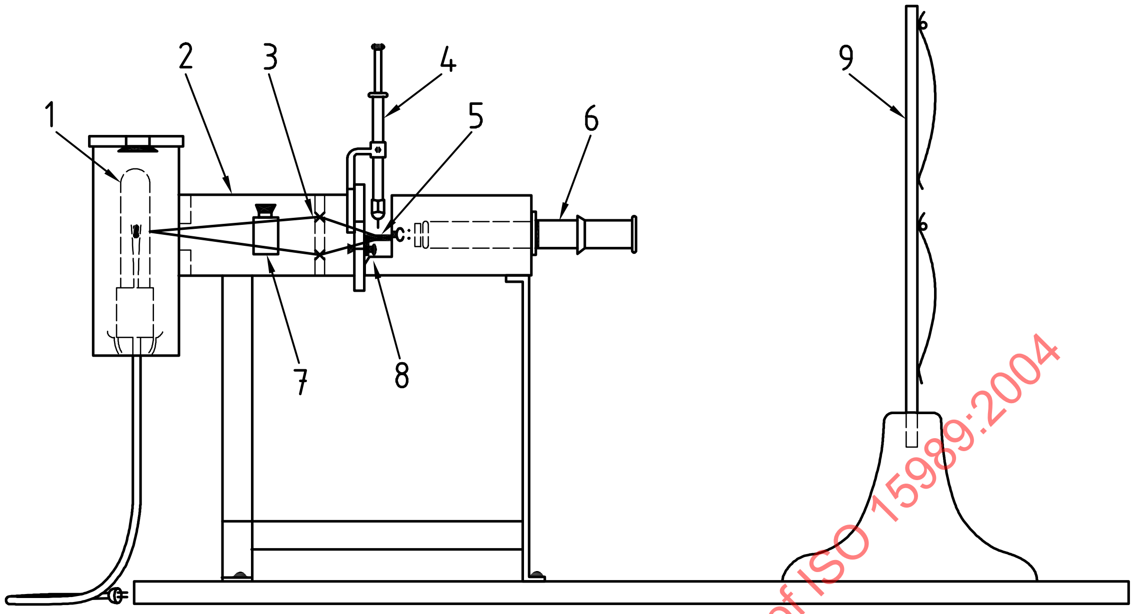
5.2 Droplet image projection apparatus

Alternatively, a droplet-projection contact-angle meter (see Figure 1) may be used. It shall be capable of projecting the image of a droplet of liquid on the surface of the substrate onto a screen so that the angle of the tangent to the droplet at the substrate surface can be measured. The apparatus shall consist of the following elements:

5.2.1 Angle-measuring instrument, such as a protractor or similar device, for measurement of the contact angle.

5.2.2 Filter, used to reduce the heat falling on the specimen and the droplet.

5.2.3 Ventilated lamp house, containing a light source.



Key

1 250 W projection lamp
2 tube
3 lens
4 hypodermic syringe
5 specimen
6 microscope
7 water cell
8 horizontal specimen stage
9 frosted-glass screen

Figure 1 — User-constructed droplet-projection contact-angle meter

5.2.4 Microscope draw tube, suitable for projecting the image of the droplet onto a screen with an enlargement of ×25.

5.2.5 Frosted-glass screen, onto which the droplet image is projected.

5.2.6 Horizontal specimen stage, capable of accommodating the test specimen, and with a means of adjusting the stage vertically.

5.2.7 Tube, containing a lens to concentrate the beam of light.

5.2.8 Hypodermic syringe, capacity 1 ml, fitted with a flat-tipped 27 gauge stainless-steel needle and capable of providing 150 to 200 droplets.

5.3 Computer-based systems

PC-based systems with automatic image analysis capabilities are available for contact-angle measurements. These systems provide a greater degree of accuracy in comparison to the droplet-projection system.

6 Test liquid

Use distilled water or ultra-pure water (as used for HPLC). Keep the water in a clean container.

NOTE 1 Reagent-grade deionized water may also be used, but the results will not be as accurate.

NOTE 2 Any contamination introduced into the water will affect the results.

7 Test specimens

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

7.2 Extreme care shall be taken to prevent the surface of the specimen from being touched or handled in the areas in which the test is to be made.

7.3 The number of measurements per specimen shall be determined using published tables for sampling plans. The recommended number of readings per specimen is ten.

NOTE Complete tables can be found in most books on quality control. See e.g. J.A. Duncan, *Quality Control and Industrial Statistics*, 3rd ed., Irwin, Homewood, IL, USA, 1965.

7.4 For the purpose of determining the wetting-tension profile across the width of the roll, contact-angle measurements can be made at intervals of one specimen length (i.e. approximately 300 mm) across the width of the roll.

8 Conditioning

8.1 Conditioning is not generally required for routine quality assurance or process control measurements as it will affect the measured value which will no longer be representative of the actual conditions.

8.2 Conditioning is required for interlaboratory measurements intended to compare results. In such cases, condition the specimens at 23 °C $\pm$ 2 °C and (50 $\pm$ 5) % relative humidity for not less than 40 h prior to testing. In cases of disagreement, the tolerances shall be $\pm$ 1°C and $\pm$ 2 % relative humidity. Whenever possible, conduct testing under the same conditions as used for conditioning.

9 Test conditions

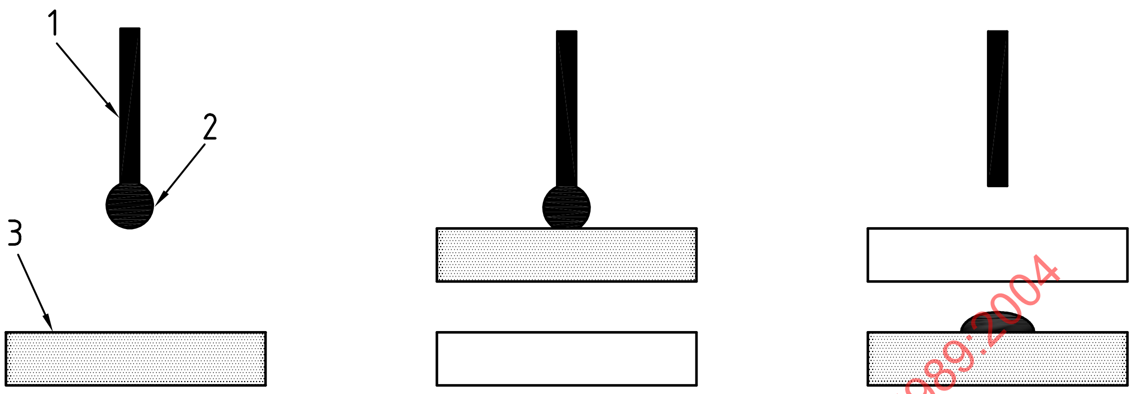
Special test conditions are not generally required for routine quality assurance.

10 Procedure

10.1 Place a specimen on the specimen holder of the instrument. Make sure the specimen is lying flat without wrinkles and distortions.

10.2 Suspend a 1 µl to 2 µl droplet of water (see Clause 6) at the end of the syringe needle. Bring the surface of the mounted specimen into contact with the pendant droplet. Then move the surface of the specimen away to complete droplet transfer (see Figure 2). Do not drop or squirt droplets on to the specimen surface.

NOTE Larger, 5 µl to 8 µl, droplets may be used. However, larger droplets may lose their spherical shape, resulting in some degree of error.



a) Droplet on syringe **b) Droplet transfer** **c) Droplet on surface**

Key

1 syringe needle

2 water

3 specimen surface

Figure 2 — Water droplet transfer technique

10.3 Use one of measurement techniques a), b) and c) described below to determine the contact-angle value. Follow the instrument manufacturer's instructions concerning the maximum time between transferring the water droplet and measurement, if specified. If not specified, make the measurement within 1 min $\pm$ 10 s of droplet transfer.

a) Measure the contact angle directly with a protractor, aligning the protractor cursor line with the tangent to the droplet at the specimen surface.

b) Measure the angle between the specimen surface and the line from the three-phase point to the apex of the droplet. Multiply the number obtained by 2 to give the contact angle.

NOTE This technique is the subject of US Patent 5,268,733. ISO is not in a position to give any authoritative or comprehensive information about this patent. Users of this International Standard are expressly advised that determination of the risk of infringement of this patent is entirely their own reponsibility.

c) Determine the angle from the dimensions of the droplet image in accordance with ASTM D 724 or ASTM D 5946:

$$\theta = 2 - \arctan(H/R)$$

where

θ is the angle of contact of the droplet with the specimen surface;

H is the height of the droplet image;

R is half the width of the droplet image.

NOTE 1 Method a) is biased due to the subjective nature of finding a tangent to the droplet image at the three-phase point. If method a) is used, the bias of each operator's measurements should be determined. Methods b) and c) are generally free of bias.

NOTE 2 The algorithms used in methods b) and c) assume a spherical droplet configuration and are most accurate for small droplets ($\leqslant$ 1 µl in volume).

10.4 Advance the specimen to place the next droplet on a previously untouched area.

10.5 Make preferably ten contact-angle measurements on the specimen.

11 Calculation and interpretation of results

11.1 Calculation

11.1.1 Calculate the average of the measurements.

11.1.2 Calculate the standard deviation of the measurements.

EXAMPLE

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

The average contact angle is 70°. This result corresponds to the lower end of the very high treatment level. The standard deviation is 2,4°.

11.2 Interpretation of the results

Using Table 1, find the range of wetting-tension values which corresponds to the range of measured contact-angle values.

NOTE In the conversion chart in Table 1, the contact angle of 70° calculated in the example above corresponds to an approximate wetting tension of 41 mN/m.

Table 1 — Conversion of contact angle to wetting tension

Contact angle rad (deg)	Approximate wetting tension (surface tension) mN/m
0,89 (51)	53
0,91 (52)	52
0,93 (53)	52
0,94 (54)	51
0,96 (55)	50
0,98 (56)	50
0,99 (57)	49
1,01 (58)	49
1,03 (59)	48
1,05 (60)	47
1,06 (61)	47
1,08 (62)	46
1,10 (63)	46
1,12 (64)	45
1,13 (65)	44
1,15 (66)	44
1,17 (67)	43
1,19 (68)	42
1,20 (69)	42
1,22 (70)	41
1,24 (71)	40
1,26 (72)	40
1,27 (73)	39
1,29 (74)	39
1,31 (75)	38
1,33 (76)	37
1,34 (77)	37
1,36 (78)	36
1,38 (79)	36
1,40 (80)	35
1,41 (81)	34
1,43 (82)	34
1,45 (83)	33
1,47 (84)	32
1,48 (85)	32
1,50 (86)	31
1,52 (87)	30
1,54 (88)	30
1,55 (89)	29
1,57 (90)	29
1,59 (91)	28
1,61 (92)	27
1,62 (93)	27
1,64 (94)	26
1,66 (95)	25
1,68 (96)	25
1,69 (97)	24
1,71 (98)	24
1,73 (99)	23
1,75 (100)	22

12 Precision

An interlaboratory study was conducted in 1995 in accordance with ASTM E 691 involving four materials and eight laboratories in the US[1)]. The results are given in Table 2. Each test result was the average of ten individual determinations. Each laboratory obtained three test results for each material on two days.

Table 2 — Interlaboratory study results

Material	Treatment power watts/sq.ft./min	Average contact angle degrees	Repeatability standard deviation, s_r	Reproducibility standard deviation, s_R
HDPE film with EVA backing	10	68,99	1,608 44	2,840 39
HDPE film with EVA backing	2	69,39	2,416 52	3,110 40
HDPE film with EVA backing	1	75,03	2,157 06	3,080 72
Polypropylene film	Pre-treated	85,00	1,959 80	4,032 18

NOTE 1 The data demonstrate that the precision of the results is generally independent of the treatment level (wetting tension) of the film.

NOTE 2 The data in this table shall not be rigorously applied to the acceptance or rejection of material, as the data are specific to the interlaboratory study and are not representative of other lots, conditions, materials or laboratories. Users of this test method shall apply the principles outlined in ASTM E 691 to generate data specific to their laboratory and materials, or between specific laboratories.

NOTE 3 Instrument error depends on the instrument used. Instrument error can be assessed by measuring a uniform surface and by calculating the standard deviation of the measurement.

NOTE 4 These data were developed utilizing all three of the measurement procedures described in 10.3.

13 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) details of the test specimen and its condition;

c) details of any conditioning of the specimen;

d) the name of the instrument used;

e) the maximum time between transferring the water droplet and making the measurement;

f) the number of contact-angle measurements made;

g) the average value of the contact-angle measurements;

h) the standard deviation;

i) the corresponding wetting tension from the conversion chart (see Table 1);

j) any comments and observations;

k) the date of the test.

1) Supporting data are available from ASTM headquarters. Request RR:D20-1214.

Annex A
(informative)

Significance and use of contact-angle measurements

A.1 The ability of polymer films to retain inks, coatings, adhesives, etc., is primarily dependent upon the character of their surfaces, and can be improved by one of several surface-treatment techniques. Electrical-discharge treatment, such as corona treatment, has been found to increase the wetting tension of a polymer film surface by increasing the surface polarity. The stronger the treatment, the higher the polarity. The higher the polar component, the more actively the surface reacts with different polar interfaces. It is therefore possible to relate the wetting tension of a polymer film surface to its ability to accept and retain inks, coatings, adhesives, etc., if the ink, coating or adhesive contains the necessary polar functionality. Wetting tension in itself is not a completely acceptable measure of ink, coating or adhesive adhesion.

A.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 measurably change shape in reaction to surface energy. Many indirect methods have been proposed[2]. Different test methods tend to produce different results on identical samples. Practical determination of a solid's surface energy utilizes this interaction of the solid with test liquids.

A.3 Although in the industry the level of surface treatment of polymer films has been traditionally defined in terms of dyne/cm (mN/m), these values are derived from a subjective interpretation of the observed test liquid behaviour.

A.4 The surface energy of a solid material consists of two components, dispersive and polar. Water will interact with different polymers, treated or untreated, according to the polar and dispersion forces acting upon it, but will not chemically react with the polymer. A water droplet will assume a shape in response to the surface energy and polarity of the film's surface. As a result, different polymers which are treated to different levels can be considered a homologous series in terms of their interaction with water. So each time a film is subjected to corona treatment, a new member of the homologous series of polymers is produced. For such a series, the water droplet will assume a shape in response to the particular surface energy and polarity of the film's surface.

For such a series, an empirical equation exists which describes a relationship between the wetting tension and the cosine of contact angles of a test liquid, such as water. This equation can be used to estimate the wetting tension of the substrate from the water contact-angle values (see Annex C).

A.5 The conversion chart for estimating the approximate wetting tension for a particular substrate from the contact-angle values is shown in Table 1. This conversion chart is shown for the purpose of providing a “bridge” between previous test data obtained using the test method in ASTM D 2578[3]. Otherwise, contact-angle values have to be used to define the film's surface. Because this International Standard and ASTM D 2578 employ different test liquids, it is impossible to equate a water contact-angle value to a single wetting-tension value. For the purpose of this International Standard, each water contact-angle value is equated to a range of wetting tension values.

2) S. Wu, *Polymer Interface and Adhesion*, Marcel Dekker, Inc. New York, 1982.

3) Equivalent to ISO 8296, *Plastics — Film and sheeting — Determination of wetting tension*.

A.6 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	$> 90^\circ$	(less than approx. 34 dyne/cm)
Low level of treatment	85° to 90°	(approx. 36 dyne/cm to 34 dyne/cm)
Medium level of treatment	78° to 84°	(approx. 39 dyne/cm to 36 dyne/cm)
High level of treatment	71° to 77°	(approx. 43 dyne/cm to 40 dyne/cm)
Very high level of treatment	$< 71^\circ$	(above approx. 43 dyne/cm).

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

A.7 Almost all materials have variations in surface energy as one moves from point to point. Non-uniform treatment of film with corona treaters may also add variability to the results. Therefore, the surface energy of a specimen should be described by the average wetting tension and its variability over the sample surface.