INTERNATIONAL STANDARD

ISO 16365-3

First edition
2014-05-01

Plastics — Thermoplastic polyurethanes for moulding and extrusion —

Part 3: Distinction between ether and ester polyurethanes by determination of the ester group content

Plastiques — Polyuréthannes thermoplastiques pour moulage et extrusion

Partie 3: Distinction entre polyuréthannes éther et ester par dosage des groupements esters

Reference number
ISO 16365-3:2014(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

ISO 16365 consists of the following parts, under the general title *Plastics — Thermoplastic polyurethanes for moulding and extrusion*:

— *Part 1: Designation system and basis for specifications*

— *Part 2: Preparation of test specimens and determination of properties*

— *Part 3: Distinction between ether and ester polyurethanes by determination of the ester group content*

Introduction

The saponification value is a fast and easy determination method to distinguish between polyesterol and polyetherol-based thermoplastic polyurethanes. However, the saponification value strongly depends on the reaction conditions. Higher saponification values result in longer hydroxylation times and/or higher temperatures. With this procedure, the theoretically expected values have been found.

Plastics — Thermoplastic polyurethanes for moulding and extrusion —

Part 3: Distinction between ether and ester polyurethanes by determination of the ester group content

1 Scope

This part of ISO 16365 specifies a method for the determination of esters including ester thermoplastic polyurethanes (TPU) and ether TPU for quality control without the necessity of sophisticated instrumentation and avoids or minimizes long-term microbial testing for TPU materials. The method described is used to distinguish major TPU types and characterize TPU mixtures.

The method is applicable to all linear polyurethanes based on 4,4'-diphenylmethane diisocyanate (MDI) and is intended for instance to minimize long-term tests related to microbe resistance and hydrolysis.

2 Normative references

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

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

3.1
acid value of total hydrolysable groups
S_{Z1}
number of milligrams of potassium hydroxide required to neutralize the free acids of ester and urethane groups present in 1 g of thermoplastic polyurethanes, when determined in accordance with the procedure specified in this part of ISO 16365

Note 1 to entry: The acid value is expressed in milligrams per gram.

3.2
acid value of hydrolysable urethanes
S_{Z2}
number of milligrams of potassium hydroxide required to neutralize the free acids of only urethane groups present in 1 g of thermoplastic polyurethanes, when determined in accordance with the procedure specified in this part of ISO 16365

Note 1 to entry: The acid value is expressed in milligrams per gram.

3.3
ester content
E
number of milligrams of potassium hydroxide required to neutralize the free acids of only ester groups present in 1 g of thermoplastic polyurethanes, when determined in accordance with the procedure specified in this part of ISO 16365

Note 1 to entry: The ester content is expressed in milligrams per gram.

4 Principle

The content of ester groups in TPU is determined by alkaline hydrolysis. The amount of urethane groups is determined and subtracted from the determined total amount of hydrolysable compounds, i.e. esters and urethanes. The difference is a measure of the content of ester groups in mg KOH/g. Pure polyether-TPU yields results close to 0 mg KOH/g.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 Dimethylsulfoxide.

5.2 Potassium hydroxide solution, c(KOH) = 0,5 mol/l accurate to 0,001 mol/l, methanol solution.

5.3 Sulfuric acid, $c(H_2SO_4)$ = 0,5 mol/l accurate to 0,001 mol/l, aqueous solution.

5.4 Phenolphtaleine, 1 % in methanol or ethanol.

5.5 Methanol, for analysis.

5.6 Water, distilled or of equivalent purity in accordance with ISO 3696.

6 Apparatus

6.1 Centrifugal mill, with sieve of 2 mm.

6.2 Analytical balance, accuracy 0,1 mg or better.

6.3 Erlenmeyer flask, with capacity of 250 ml which can be closed.

6.4 Automatic burette, with capacity of 20 ml or similar.

6.5 Magnetic stirrer, with heater.

6.6 Reflux cooler, with polytetrafluoroethylene (PTFE) manchette.

6.7 Magnetic stirrer, 40 mm.

6.8 Volumetric measuring cylinder, 50 ml.

6.9 Soxhlet apparatus.

7 Sample preparation

Cut a representative fraction of the sample to be analysed into pieces of approximately 2 mm in diameter.

For thermoplastic urethane materials containing phosphorous plasticizers, extract 3 g of the powdered sample for 4 h in methanol using a Soxhlet extractor (see 6.9). Remove the sample from the extractor and dry for 30 min at 60 °C in an oven.

NOTE Phosphorous esters used as plasticizers for TPU have no influence on the resistance of the material against microbes. However, the presence of phosphorous ester will cause a higher ester content result.

8 Procedure

At least two determinations shall be carried out.

Weigh a test portion of 0,5 g to the nearest 1 mg (E gram) into an Erlenmeyer flask of 250 ml (see 6.3). Add 40 ml dimethylsulfoxide (see 5.1) and a magnetic stirrer (see 6.7), close the flask and the stir for 15 min.

NOTE The sample may only be partially dissolved after 15 min.

Add 20 ml (see 5.2) of a solution of potassium hydroxide (see 5.2) under continuous stirring to avoid coagulation. The sample is hydrolysed for 5 h under reflux conditions and continuous stirring (see 6.6) on the magnetic stirrer with heater (see 6.5).

Two blank determinations are prepared following the same procedure.

Cool to room temperature and rinse the reflux cooler and Erlenmeyer wall with 50 ml of water. The surplus amount of KOH is titrated by sulphuric acid (see 5.3) from red to colourless using 10 droplets of phenolphthalein solution as indicator (sample: V_1 ml, average blanks; V_{1b} ml) but avoiding an excess of sulphuric acid.

After titration add 10 ml of H_2SO_4 (see 5.3) by a burette and boil for 10 min on the magnetic stirred with heater while continuously stirring. It is essential that all carbon dioxide is removed from the solution.

After cooling to room temperature the surplus amount of sulphuric acid is titrated back by KOH (see 5.2) using phenolphthalein as indicator. The titration is carried out from colourless to slightly pink (sample: V_2 ml, average blanks: V_{2b} ml).

NOTE 1 Fillers like $CaCO_3$ and other additives such as some flame retardants which may form salts might have an effect on the result.

NOTE 2 Pigments may change the visibility of the colour change of the indicator which will make it difficult or impossible to carry out a visual titration.

NOTE 3 Potentiometric titration is also possible.

9 Calculation

Calculate the ester content in mg KOH/g as follows:

$$E = S_{Z1} - S_{Z2} \tag{1}$$

where

E is the ester content in mg KOH/g.

$$S_{Z1} = \frac{(V_{1b} - V_1)}{w} \times 56{,}1 \frac{\text{mgKOH}}{\text{ml}} \times t_{H_2SO_4} \tag{2}$$