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Methods for the prediction of thermophysical properties of polyurethane raw material mixtures

Stephanie Peper [a, *], Ralf Dohrn [a], Klaus Konejung [b]

[a] Bayer Technology Services GmbH, Downstream Processes, Geb. B310, D-51368 Leverkusen, Germany
[b] Covestro AG, Polyurethanes, Global Technical Product Management PET, Geb. B211, D-51365 Leverkusen, Germany

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ABSTRACT

According to the world wide safety standards, a classification for transport and handling is required for every single mixture. To reduce the experimental effort to determine physical properties for the classification of multicomponent mixtures of polyurethane raw materials, existing predictive methods for the initial normal boiling point and for the flash point have been extended based on group contribution methods like UNIFAC and modified UNIFAC (Dortmund). A new predictive method for the auto ignition temperature has been developed. The calculation results were evaluated based on experimental data for more than 1500 mixtures. It could be shown that these approaches can be reliably applied for the classification of multicomponent mixtures of polyurethane raw materials.

1. Introduction

Whereas the number of raw materials for the production of polyurethanes is huge, the number of mixtures and formulations is abundant. Depending on applications and their specific requirements on physical and chemical properties, reactivity of the components and also the processing equipment dedicated mixtures of polyols or isocyanates are created, containing catalysts, stabilizers, foaming agents or defoamers, crosslinkers or chain stoppers and other components. This can end up with more than 20 pure components ranging from 18 g/mole for water to 100 kg/mole for liquid silicones. According to the world wide safety standards, a classification for transport and handling is required for every single mixture. Within the *Globally Harmonized System of Classification and Labeling of Chemicals* (GHS), which has been implemented worldwide by the United Nations [1], the thermophysical properties of substances and mixtures are the basis for their classification concerning physical hazards. According to the GHS classification, a flammable liquid is a liquid with a flash point of not higher than 200 °F (93.33 °C or 366.48 K). Criteria for the assignment of a flammable liquid to one of the four defined categories are the flash point and the initial normal boiling point. For example, flammable liquids of category 1 have a flash point lower than 23 °C (296.15 K) and an initial normal boiling point not higher than 35 °C (302.15 K). Aside from experimental testing or literature search, GHS allows data to be calculated [1]. Besides GHS, for dangerous goods identical physical limits are used for the transport classification, but in this case the corresponding physical properties have to be determined experimentally. We use the calculation results to decide whether the mixture is a dangerous good or not.

Within the last 20 years Bayer has tested physical properties for more than 1500 multicomponent mixtures with defined compositions. This large data base has been used to evaluate the calculation methods developed in this work.

The mixtures are.

- Polyol formulations with big differences of the molecular weight of the components consisting mainly of polyether or polyester polyols mixed with stabilizers, catalysts, foaming agents, flame retardants or chain extenders
- Isocyanate mixtures containing monomeric or polymeric isocyanates as well as prepolymers and small amounts of stabilizers

* Corresponding author.
E-mail address: Stephanie.Peper@bayer.com (S. Peper).

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– Additive mixtures consisting of different components with low molecular weight.

The typical ingredients of these mixtures are summarized in Table 1.

In this work we evaluated methods for the calculation of the initial normal boiling point [2], the flash point [3,4], and the auto ignition temperature [5–7]. The methods are predictive and require as input data only the composition of the mixture and only usually accessible properties of the pure-components (molecular weight [8–11], molecular structure, vapor pressure curve [8,11–13], including normal boiling point, flash point [8,11,13], heat of combustion [8,14], heat capacity [8], and auto ignition temperature [8,11,12,15]).

2. Initial normal boiling point

The initial normal boiling point is defined as the temperature at which the vapor pressure of a liquid is equal to the standard pressure (101.3 kPa). The initial normal boiling point of a pure substance should be determined experimentally because estimation methods for vapor–pressure curves and normal boiling points, respectively, do not usually satisfy the requirements regarding the precision. If pure-component data are available and interactions between the components of a mixture are known, the boiling point of mixtures can be calculated applying standard equilibrium thermodynamics.

2.1. Experimental methods

The initial normal boiling point can be determined experimentally with several methods. The most common methods are the usage of an ebulliometer, the dynamic method, the distillation method, the method according to Siwoloboff, photocell detection, differential thermal analysis or differential scanning calorimetry. Using an ebulliometer the liquid is heated at atmospheric pressure until it boils. The determined temperature of the liquid, corrected to standard atmospheric pressure, corresponds to the normal boiling point. Applying the dynamic method, the vapor recondensation temperature in the reflux is measured. Similar to the dynamic method applying the distillation method, the vapor recondensation temperature is related to the boiling point. Using the method according to Siwoloboff, a sample is heated in a sample tube which is immersed in a heat-bath liquid. The boiling temperature corresponds to the temperature at which a regular string of bubbles escapes from the capillary or to the temperature at which the string of bubbles stops and the fluid suddenly starts rising in the capillary. The photocell detection method is based on the same principle as the Siwoloboff method with the difference that the rising bubbles are detected photo-electrically [16].

If not pure substances but mixtures are investigated, the obtained results have to be interpreted with care. If, e.g., a sample includes low-boiling substances, the emergence of a low-boiling component will be registered as the boiling point. Repeated determinations with the same sample can change the composition from measurement to measurement which results in an increasing value of the determined boiling point. If liquids with a tendency to superheat are investigated, often too high boiling points are found. For this type of compounds, distillation methods or the dynamic method are more suitable than the other methods.

According to the GHS regulations [1], the initial normal boiling point of flammable liquids should be determined as described in ISO 3924, ISO 4626 or ISO 3405. ISO 3924 describes a chromatographic method. Applying this method, the chromatographic system is calibrated with a mixture of hydrocarbons of known boiling points covering the range of the sample. The calibration curve is related to the boiling points, the retention times and the peak areas of the components of the calibration mixture. The initial normal boiling point of the sample under investigation is equal to the temperature corresponding to the retention time at which the cumulative corrected area count is equal to 0.5% of the total sample area under the chromatogram obtained under the same chromatographic conditions as the calibration was performed. ISO 4626 and ISO 3405 describe distillation methods where the initial normal boiling point is defined as the temperature of the vapor noted at the moment when the first drop of condensate falls from the tip of the condenser during a distillation carried out under standardized conditions, whereby the location of the temperature sensor is assigned to be in a defined position.

2.2. Calculation of the initial normal boiling points of mixtures

As mentioned above, the boiling point of mixtures can be calculated applying standard equilibrium thermodynamics when pure-component data are available and interactions between the components of a mixture are known. Boiling occurs when the vapor pressure of the mixture is equal to the pressure of the surrounding atmosphere; in case of the normal boiling point the pressure is

Table 1
Typical ingredients of polyurethane raw material mixtures used in this work.

Ingredient	Description	Numb. Of elements[a]	Molecular weight (g/mol)
Isocyanates	di- or polyisocyanates or isocyanate prepolymers	20	178 to 5000
Polyetherpolyol	Monomeric diols, triols up to polyols with 8 hydroxyl groups, e.g., sucrose or amines polymerized with propylene oxide or ethylene oxide	150	100 to 10000
Polyesterpolyol	Aliphatic or aromatic diacids polymerized with aliphatic diols or triols	30	500 to 2000
Chain extenders	Mono- or dimeric diols, triols up to sugars with 8 hydroxyl groups	20	60 to 350
Amine catalysts	Secondary or tertiary amines	30	100 to 700
Metal catalysts	e.g. potassium acetate, dibutyltin dilaurate (DBTL)	5	100 to 1000
Stabilizers	Polyether Polysiloxanes	50	500 to 100000
Flame retardants	e. g. Trichloropropylphosphate (TCPP), triethyl phosphate (TEP)	5	100 to 500
Anti-oxidants	Tocopherol, Butylhydroxytoluene,	10	200 to 500
Other additives	Hydrocarbons, alkylbenzenes	10	50 to 200
Blowing agents	HFCKWs, alkanes like isobutane or pentanes	5	70 to 400
Water	Water as blowing agent	1	18
Inertial fillers	Mineral powder or fibers, glass fibers, hollow glass bubbles, anorganic pigments, carbon black	20	Not applicable

[a] Number of components belonging to this class from the overall list of pure components … .