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Test Method

Development and validation of a novel rheological test device and measurement system for determining the influence of humidity on viscosity

E. Dohmen [a, b, *], R. Füßel [a], M. Müller [a], M. Schäffler [c], M. Gude [a]

[a] Technische Universität Dresden, Institut für Leichtbau und Kunststofftechnik, 01062 Dresden, Germany
[b] Technische Universität Dresden, Institut für Magnetofluiddynamik, Mess- und Automatisierungstechnik, 01062 Dresden, Germany
[c] Anton Paar GmbH, Ostfildern-Scharnhausen, 73760, Germany

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ABSTRACT

Although a strong impact of humidity on polymers and the formation of their molecular network is known, the complex interactions between humidity, temperature, diffusion, reaction kinetics, rheological behaviour and mechanical properties are not fully understood yet. Most current approaches solely analyse the relationships between environmental conditions in a solidified or crosslinked state and the mechanical properties. In contrast, this work focusses on measuring changes in rheological properties depending on relative humidity in the liquid state. A custom designed novel measuring geometry is introduced and validated. It enables for the first time to rheometrically investigate the influence of relative humidity on reactive systems during their cross-linking process. Our results significantly depict the influence of humidity on the cross-linking process and the gel time. The potential of the introduced measuring geometry for improving reactive systems, adapting these precisely to environmental boundary conditions or assuring product performance is hereby demonstrated. This is especially important for industrial manufacturing processes running at different production sites around the world in different climatic zones or repair processes being performed outdoor, e.g. for wind energy plants.

1. Introduction

Rotational rheometric experiments represent a flexible and therefore widely used characterisation method for different types of materials. Numerous industrial sectors use rheology: petro chemistry, civil engineering, food chemistry and even civil protection developed different applications. Within plastics industry the characterisation of paint, varnish, adhesives, sealants, composite resins and other polymers motivates rheological experiments due to the mechanical behaviour of such polymer materials being strongly influenced by testing temperature, states of stress and occurring frequencies [1]. Additionally, reactive polymers undergo substantial changes due to cross-linking reactions. In case of oscillatory excitation rheometric testing allows a measurement of both, the viscosity properties in the liquid state (thermoplastic melt or uncured resin) and the mechanical properties in the solid state (solidified thermoplastic or cured resin). A typical temperature range for polymer applications from −50 °C to 450 °C can sufficiently be covered by rotational rheometry.

Temperature dependent measurements are widely used to determine characteristic properties like the glass transition temperature or the point of gelation of cross-linking polymers [2]. Especially for thermoset resin systems this gives the opportunity to tailor processing precisely to meet economical or mechanical needs. The strong influence of humidity on the reaction kinetics of a polymer's network is well known [3,4]. Nevertheless just a few scientific works investigate how humidity affects the characteristic properties of polymers during their processing. Caire et al. modified a Sentmanat Extensional Rheometer (SER) for analysing mechanical properties of thermoplastic specimens depending on temperature and humidity, showing a significant influence of humidity on elongation and stress at fracture [5]. Torsional DMA measurements on gelatine and tack tests on chewing gum show a significant impact of relative humidity on the rheological properties of food materials [6]. These studies encourage further rheological

* Corresponding author. Technische Universität Dresden, Institut für Magnetofluiddynamik, Mess- und Automatisierungstechnik, 01062 Dresden, Germany.
E-mail address: eike.dohmen@tu-dresden.de (E. Dohmen).

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investigations on the humidity dependence of materials, especially for reactive systems. The above mentioned industrial sectors can benefit from the results as relative ambient humidity inevitably affects every polymer process. Subsequently e.g. bonding processes, wet lay-up composite manufacturing or reactive surface treatments can be further improved and optimised by taking into account the ambient humidity.

2. Test setup

For our investigations a commercially available environmental cell by the metrology company Anton Paar, comprising a convection oven system CTD-180HR and a humidity generator MHG 100, was used in combination with a MCR502s rheometer by Anton Paar. This device allows rheological or dynamic mechanical analysis under controlled humidity and temperature conditions. Anton Paar additionally offers a special ring geometry for improved moisture penetration. As the environmental setup is fully integrated into the rheometer control software test sequences may be programmed precisely, allowing a variation of relative humidity at constant temperature or a variation of temperature at constant relative humidity. The desired moisture content is adjusted by a separate humidity generator and transferred into the humidity chamber as shown in Fig. 1. Temperature is controlled by Peltier elements integrated into the environmental chamber, which are specially designed to avoid condensation for high values of relative humidity at low temperatures. With this device measurements can be performed in a temperature range from 5 °C to 120 °C and in a range of relative ambient humidity from 5% to 95%, depending on the respective corresponding parameter. For reactive systems different disposable measuring system, for example with a 25 mm plate to plate geometry D-PP-25, are available by Anton Paar. For the environmental cell Anton Paar offers the reusable plate to plate ring geometry PPR-3228, designed with an increased surface-to-volume ratio for improved moisture penetration.

The measuring geometries analysed within this work are listed in Table 1. Geometry D-PPR-3020 shown in Fig. 2 is a custom design by the authors being a compromise regarding ease of gap filling, measurement precision, utilisation of disposable measuring geometries for reactive systems, improved moisture penetration and cost reduction. It is compatible with the measuring axis D-CP/PP-7 by Anton Paar for disposable measuring systems. Ring-plate measuring systems are preferable for humidity measurements as moisture pick up is possible from inside and outside simultaneously so diffusion depth is reduced resulting in shorter diffusion times. In addition stress distribution is more homogeneous due to the reduced radial gradient and due to reduced internal stresses resulting from chemical or physical shrinkage. For our measurements the geometries D-PP-25, PPR-3228 and D-PPR-3020 were equipped with an additionally custom designed “umbrella” (shown in Fig. 2) unless otherwise stated. This “umbrella” is mounted at the measuring axis D-CP/PP-7 to prevent droplets of condensed water from dripping into the disposable sample holder.

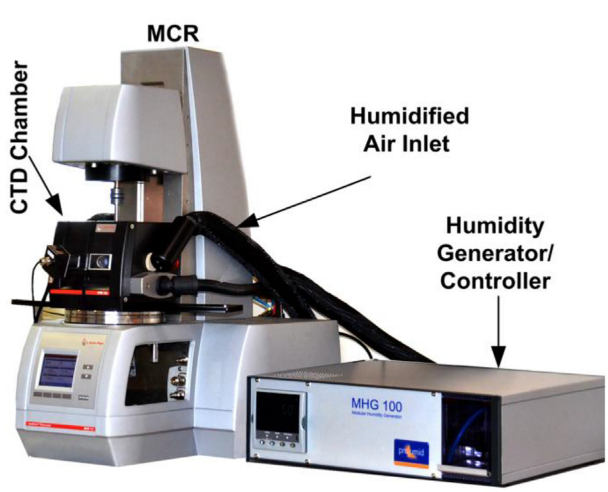

Fig. 1. Anton Paar MCR Rheometer equipped with Peltier heated convection chamber and humidity generator.

3. Materials

For validating the developed measuring geometry D-PPR-3020 a silicon oil Elbesil B1000 was utilised as reference material. For further experiments a bisphenol A (Fig. 3) based epoxy resin Epilox© 19-03 and isophorone diamine (IPD) (Fig. 4) hardener, both supplied by Leuna Harze GmbH, was investigated. The mixing ratio of resin component to the hardener component was 100:27.7 in mass parts.

It is known from previously published work that epoxy networks exhibit strong dependence on water, both, during processing [4] and after cross-linking [7]. The degree of interaction is dominated by the composition of the constituents and the free volume content. Hydrophilic groups like -NH_2 and -OH tend to promote the reaction with water [8]. As pointed out in Ref. [7] it is important to distinguish between free water molecules and water forming hydrogen bonds within the epoxy network. Hence we expect a strong dependence on the relative humidity on the cross-linking behaviour during testing the described epoxy system.

4. Experimental

The experimental section is divided in two parts. Firstly the developed measuring geometry D-PPR-3020 was validated utilising the silicon oil and different established measuring geometries as reference. Based on these results subsequent experiments with the novel measuring geometry D-PPR-3020 were performed for the selected epoxy resin system.

Validation of the developed measuring geometry D-PPR-3020 was performed at different humidity levels, where the reference was a CP-25 cone to plate measuring geometry. Humidity shows no significant influence on the rheological properties of Elbesil B1000 during the observed measuring period. For the evaluated measuring geometries slight differences in complex viscosity are observed as to be seen in Fig. 5. Referring to Table 2 for PPR-3228 a remarkable offset of the mean complex viscosity of approx. 300 mPa s compared to the CP-25 measuring geometry as well as an increased standard deviation of 3.1% are recognised.

As D-PPR-3020 is disposable and improved for moisture penetration it enables measurements on reactive systems for different environmental conditions. The influence of relative ambient humidity on the epoxy resin Epilox© 19-03 was hereinafter experimentally determined. Therefore progressive steps were performed increasing relative humidity (RH) in the test chamber. Starting from 10% RH the ambient humidity was stepwise increased by 20% RH up to 70% RH unless otherwise indicated. These progressive experiments were performed at 23 °C.

In Fig. 6 the experimental results for the pure resin component of Epilox© 19-03 are displayed, showing no significant influence of humidity on the complex viscosity. In contrast to this, the hardener component shows an instantaneous decrease in complex viscosity below the lower measuring range when increasing RH from 10% to 30% (Fig. 7). For the reactive mixture of Epilox© 19-03 resin and hardener initial complex viscosity is an order of magnitude higher