Measurement possibilities of water content in polyamide

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Abstract. Water content of polyamide is an important parameter, because it has great effect on the elongation, toughness and impact strength. The aim of our research was to determine moisture in polyamide-6 and polyamide-6.6 granules with different pretreatment of the base material. The specimens were prepared and conditioned in distilled water or non-conditioned. Thermogravimetric analysis, moisture analysis and coulometric Karl-Fisher indirect titration were used for the determination of humidity content. We used polyamide granules and flakes, and polyamide nanocomposites filled with montmorillonite for the water content measurements. First, we compared the technics and chose the most applicable to measure the water content in the samples, and made further measurement of polyamide nanocomposites.

1. Introduction
Automotive industry widely used polyamide (PA) and their composites in automotive structure applications [1–3]. Angioplasty balloon also made from polyamide, used as medical application [4]. In polymer processing moisture content is a distraction, so polymer granules need to be dried before the process. If the basic material is polyamide, it is necessary to make a conditioning procedure after polymer processing, like injection moulding or extrusion. The water absorption of polyamide strongly influences on its mechanical properties [3, 5, 6]. The amide bond can bind the water by H-bond. Our previous research investigated polyamide nanocomposites, reinforced with montmorillonite (MMT) nanoclay [7]. MMT can reduce the water absorption in polyamide [8], and in the same time it can increase mechanical properties, like tensile and impact strength [9, 10]. In our experience, MMT do not always improve the tensile and impact strength. We used pure polyamide-6 and polyamide-6.6 reinforced with 30% glass fiber (GF) materials, and made 1 wt%, 2 wt%, and 5 wt% of MMT PA-nanocomposites. It showed that the MMT could not cause more reinforcing properties besides glass fiber reinforcement.
2. Experimental

2.1. Materials
The examined raw materials were PA-6 (Grilon BS produced by EMS Chemie), and PA-6.6 with 30% GF reinforced (Zytel 70G30HSL produced by DuPont). The MMT was Nanomer I.30P (produced by Nanocor USA) a surface modified nanoclay. The surface modifier was octadecyl ammonium.

2.2. Measurement methods and technics of moisture absorption in polyamide

2.2.1. Method 1: PA-6 was used in all measurements to investigate the measurement technics to determine the moisture content. One of the PA-6 base material was flattened (it means the normal granules was flattened with a mill) and the other was normal granules. The two different shape granules were conditioned by distilled water for 2 days or non-conditioned. The non-conditioned granules were stored in air for 2 days.

2.2.2. Method 2: Six new nanocomposites were prepared with surface modified MMT. The PA-6 and PA-6.6 with 30% GF were mixed with 1 wt%, 2 wt% and 5 wt% MMT content [7]. A small amount (ca. 10 g) of each composite granulate were conditioned in Weiss Umwelttechnik GmbH WK11-340/40 climate chamber for seven days on a temperature of 70±1 °C with relative humidity of 62±1%.

2.2.3. Measurement technics 1: TGA Q50 thermogravimetric analyser by TA Instruments was used first to determine the moisture content in flakes and normal granules. 5–50 mg of granulates were tested on 110 °C for 5h.

2.2.4. Measurement technics 2: Radwag MAC 50/1/NH type gravimetric moisture analyser was also used to determine the moisture content in the two different shaped granules. Ca. 10 g of granulates were tested on 150 °C.

2.2.5. Measurement technics 3: The amount of absorbed water in the granules and the six new nanocomposites was measured with Karl-Fisher (KF) titration. The testing was carried out with a Metrohm 899 coulometer, and a Metrohm 885 oven. Ca. 50 mg of granulates were tested on 170 °C.

3. Results and discussion

3.1. Comparison of the three measurement technics

3.1.1. Results of moisture content with TGA
TGA Q50 thermogravimetric analyser was used to determine moisture content in PA-6 granules. The results were shown on the Figure 1.
Figure 1. Moisture content of PA-6 granules with TGA measurement

It is showed that the flattened granules could absorb more moisture content and the granules could absorb much more water in distilled water than in the air during 2 days. The flattened granules has bigger surface, and on the surface the PA can easier absorb water then the sample inside.

3.1.2. Results with gravimetric moisture analyser
The moisture content of the samples measured by gravimetric moisture analyser. The results was showed in Table 1.

Table 1. Results of moisture content measured by gravimetric analyser

| Material: PA-6                  | Measured moisture content (%) |
|--------------------------------|-------------------------------|
| Non-cond. granules             | 1.929                         |
| Non-cond. flattened granules   | 2.067                         |
| Cond. granules                 | 7.780                         |
| Cond. flattened granules       | 8.184                         |

The moisture content results with gravimetric analyser were similar to TGA results.

3.1.3. Results of the water absorption measurements by Karl-Fisher titration
The amount of absorbed water in the granules were measured by Karl-Fisher coulometric indirect titration on the conditioned and non-conditioned flattened and normal granules. The results were showed in Table 2.
3.2. Water measurement results of PA nanocomposites

The prepared PA based nanocomposites were measured by coulometric KF titration and the results were showed in Table 3.

Table 3. Results of Karl-Fisher titration in the six nanocomposites and the base materials

| Material          | Absorbed water (%) | Water absorption of commercial material (%) |
|-------------------|--------------------|--------------------------------------------|
| PA-6              | 1.06               | 9                                          |
| PA-6 + 1% MMT     | 1.59               | 9                                          |
| PA-6 + 2% MMT     | 1.35               | 9                                          |
| PA-6 + 5% MMT     | 1.38               | 9                                          |
| PA-6.6 + 30% GF   | 0.95               | 6                                          |
| PA-6.6 + 30% GF + 1% MMT | 0.72 | 6                                          |
| PA-6.6 + 30% GF + 2% MMT | 0.76 | 6                                          |
| PA-6.6 + 30% GF + 5% MMT | 0.81 | 6                                          |

*According to the data sheet of the materials by the producers

The climate chamber was used for 7 days with 70±1 °C and with 62±1% relative humidity. It is showed that PA-6-MMT nanocomposites absorbed more water than the base material, but in the other case, PA-6.6, which has 30% GF reinforcement, absorbed less water content than PA-6.6 base material.

4. Conclusion

Three measurement technics investigated to determine moisture or water content in polyamide-6 flattened and normal granules, which were conditioned in distilled water or air. In all measurement technics the granules conditioned in water, absorbed more water. Compared the three technics we chose the Karl-Fisher indirect titration which was the most accurate technics to measure the water content in polyamide samples. We investigated the water content in six polyamide nanocomposites reinforced with montmorillonite, and the water content results showed that the nanocomposites absorbed less water next to glass fiber reinforcement than unfilled polyamide material.

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