Correlation between molar mass and thermal/mechanical properties of polyoxymethylene (POM) copolymers

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ABSTRACT

In the present study the influence of the molar mass on thermal and mechanical properties is investigated on different grades of POM (Hostaform® resins). A linear relationship between the Melt Volume Rate (MVR) and the crystallinity was found with the exception of one grade. However, the molar mass did not clearly influence other investigated properties.

INTRODUCTION, EXPERIMENTAL, RESULTS & DISCUSSION

After extensive investigations dedicated to determine the changes occurring in thermal properties like decomposition, melting and crystallisation temperature by artificial aging [1-5] of polyoxymethylene (POM) copolymer resins Hostaform® C 27021 (Ticona) and Ultraform® W2320 003 (BASF) having a similar property range, Hostaform® resins with a MVR ranging from 2,5 cm^3/10 min to 39 cm^3/10 min were investigated. The MVR and the average molar mass of a polymer are interdependent in view of the fact that usually a high MVR value corresponds to a polymer with a low relative molar mass, while a low MVR value indicates a polymer with a high molar mass [6]. Thus, it can be assumed that the investigated C 2521 grade has the highest average molar mass and the C 52021 grade the lowest among the resins under consideration. A verification was not possible due to the fact, that the institute possesses no adequate equipment like a gel permeation chromatography (GPC) device. The Hostaform® resins were supplied by Ticona both as pellets and as injection moulded shouldered bar test specimens according to DIN EN ISO 527 [7] (dog bone). First, the characteristics of the resins were investigated as received by means of thermogravimetric analysis (TGA) coupled with mass spectrometry (MS), differential scanning calorimetry (DSC), and tensile testing.

TGA was performed using a TGA 2050 (TA Instruments) with a heating rate of 10 $K.min^{-1}$ under air atmosphere by using ceramic pans. Additionally, isothermal TGA investigations were performed under air atmosphere with a temperature of 200 °C and 220 °C.
For DSC investigations two consecutive heating runs with a rate of 10 $K.min^{-1}$ from room temperature to 200 °C were achieved by means of a DSC 2920 (TA Instruments). Between the two heating runs a cooling sequence was inserted with a rate of 10 $K.min^{-1}$ too. The samples were packed in aluminium crucibles and analysed under nitrogen atmosphere.
Tensile testing was carried out on the shouldered bar test specimens following DIN EN ISO 527. For this purpose a Zwick Z050 universal testing machine was used.

A thermooxidative ageing was realised by storing the pellets and the test specimens in an oven at 140 °C. The mass loss during the ageing procedure was monitored by weighing the bars every week until completion of the test after 8 weeks. Some bars and pellets were removed for investigations after 3 and 5 weeks. After the thermooxidative ageing the samples are investigated in terms of TGA, DSC and tensile testing under the same conditions as the non-aged samples.

Dynamic TGA results showed first that already the processing of the pellets by injection moulding – in order to obtain the test specimens - leads to a decrease in the onset temperature (T_O), and second that the thermooxidative ageing results also in a decrease in T_O (Table 1). Even after different exposure durations to thermooxidative ageing a systematic influence of the molar mass could neither be determined on the average T_O nor on the decrease of the T_O. We only found the highest T_O for the resin with the highest average molar mass and the lowest T_O for the resin with the lowest average molar mass, but there was no remarkable correlation between the T_O and the average molar mass for grades with an MVR between the two extremes.

Isothermal TGA results confirmed the consumption of the stabiliser during the first processing step since with both investigated temperatures the decrease in the duration to reach a mass loss of 3 % was the highest from the pellet state to the specimen, but again no systematic correlation could be found with regard to the average

molar mass. For the 8 weeks at 140 °C artificially aged samples we observed that some samples started to degrade before the test temperature was reached.

Table 1. T_O (°C) for a mass loss of 3 % of the different Hostaform® resins in air (heating rate 10 K/min). ΔT_O1: Onset temperature difference between initial condition and 3 weeks at 140 °C; ΔT_O2: Onset temperature difference between 3 and 8 weeks at 140 °C

grade	MVR (cm^3/10 min)	pellets (as received)	specimen initial condition	specimen after 3 weeks at 140 °C	ΔTo1	specimen after 8 weeks at 140 °C	ΔTo2
C 2521	2,5	273 ± 2,3	270 ± 0,6	265 ± 2,4	5	262 ± 1,2	3
C 9021	8	262 ± 4,0	258 ± 1,1	252 ± 1,4	6	246 ± 0,1	6
C 13021	12	263 ± 5,4	258 ± 3,3	253 ± 1,6	5	251 ± 2,4	2
C 27021	24	263 ± 3,4	258 ± 1,0	252 ± 1,2	6	245 ± 4,7	7
C 52021	39	266 ± 0,1	259 ± 7,6	255 ± 3,3	4	249 ± 2,2	6

In the DSC experiments the difference in the average molar mass resulted in a lower crystallisation temperature for the grade with the highest average molar mass and the highest crystallisation temperature for the grade with the lowest average molar mass. For the grades with intermediate average molar masses the crystallisation temperature was between the two extremes, but no systematic dependence of the crystallisation peak temperature on the average molar mass could be found. We obtained similar results for the melting peak temperature of the second heating run. With exception of grade C 13021, a linear dependence between the MVR and the crystallinity could be determined.

The results obtained by means of the tensile test showed a dependence of the modulus of elasticity from the average molar mass: grades with low average molar masses had slightly higher values than those with high average molar masses. A similar trend could be found for the strain at break. The elongation at break was higher for grades with high average molar masses. Further, the artificial ageing leaded in every case to an increase in the modulus of elasticity.

CONCLUSIONS

The investigations show that a clear influence of the average molar mass of POM copolymers on the degradation behaviour can not be proven neither in the initial state nor in an artificial thermooxidative aged state. Apparently, the stabilisation of the different grades provided by the manufacturer has a greater influence on the degradation than the average molar mass.

Kern and Cherdron [8] reported in their work that with increasing average molar mass a faster degradation has to be expected for POM homopolymers. However, the progression of the degradation in copolymers is usually stopped at the randomly distributed comonomer units in the POM chain [9]; this seems to affect the resulting degradation behaviour more than the average molar mass of the different investigated POM grades.

ACKNOWLEDGEMENT

The authors are grateful to Ticona for providing the institute with pellet and test bar specimen samples of the different POM resins for the present investigations.

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