Influence of coloration on initial material properties and on thermooxidative ageing of a polyoxymethylene copolymer

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Abstract Polyoxymethylene (POM) is a semicrystalline thermoplast of white natural colour. To meet the demands in other colours the material has to be coloured. Thus, the aim of the present study was to elaborate the influence of coloration both on the initial material properties and on the thermooxidative degradation behaviour of a POM-copolymer (POM-C). POM material with two different stabilising systems was used. A master batch on a POM substrate was added in a mass fraction of 3% to commercial distributed POM material to obtain the desired coloration. The tested specimens were injection moulded loudspeaker grills. Material properties were investigated on non-coloured and coloured samples before and after artificial ageing. The tests carried out were colour measurement, MVR (melt volume rate), mechanical testing (perforation resistance), DSC (differential scanning calorimetry) and TGA/MS (thermogravimetric analysis coupled with mass-spectrometry). Artificial ageing was realised by means of an oven storage at 140 °C for a duration up to 8 weeks to investigate the thermooxidative induced changes in the degradation behaviour. Test results showed first that the addition of a colorant had an influence on the initial properties and second that the degradation behaviour of the aged specimens depended not only on the presence of the colorant but also on the stabilising system of the material.

Introduction

Polyoxymethylene (POM) belongs to the engineering thermoplastics, it is also called polyacetal because of its basic molecular structure consisting of a repeating carbon–oxygen linkage. Acetal homopolymer refers to resin containing solely of the carbon–oxygen backbone, while for the copolymer resin the oxymethylene structure is occasionally interrupted by a comonomer unit. Acetal copolymer resin was first introduced by the Celanese Corporation in 1962. Commercial acetal copolymers are typically produced by cationic polymerisation of trioxane and a cyclic ether, such as e.g. ethylene oxide, 1,3-dioxolane or 1,3-dioxepane. Acetal copolymer resin has greater stability but reduced crystallinity as a result of carbon-to-carbon groups interspersed in its polymer chain in comparison with homopolymer resin. The polymer structure also imparts superior resistance to alkali, hot water and other chemicals, as well as long life at elevated temperatures and more latitude in processing conditions. On the other hand, its tensile strength, rigidity, softening point and melting point are all lower than those found in the acetal homopolymer [1–3]. The use of POM is growing steadily in the automotive and electronic industry. The material is supposed to replace metals in pressure loaded parts as for example window regulator or gear wheels [4].

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In the automotive industry flexibility in the coloration is an important topic to satisfy customer demands in the car indoor and outdoor colour design. As a semicrystalline thermoplast POM is naturally white opaque. Thus, to meet the demands in other colours the material has to be coloured. In practice two ways of getting coloured material can be distinguished: the first way consists in the purchase of coloured material compounded by the material producer. In this case the customer is restricted to the colour range offered by the supplier. But sometimes specific colours not typically offered by the material producer are requested, and due to the relative low sale, the coloration at the material production plant is quite cost intensive. The second way to meet specific demands in coloration is to use a non-coloured material that can be coloured during processing by the addition of master batches. This procedure has the advantage for the producer that it is on the one hand relative easy to meet customer's coloration demands even in low number of items and that he can on the other hand quickly react to fashion colour trends. The disadvantages are that master batches are expensive in comparison with commercial available coloured material and that they cannot be made up to fit every material type on the market.

The present study was undertaken to determine the effect of coloration on the initial physical and mechanical properties of POM as well as its influence on the thermooxidative ageing. According to [1] depolymerisation also known as unzipping which is one of the degradation mechanisms occurring in POM is stopped at the first comonomer unit that interrupts the carbon–oxygen backbone with a C–C-bond. Also in the case of an acidolytic or autooxidative chain scission the copolymer chains in opposition to the homopolymer chains do not unzip completely but solely to the next comonomer unit.

Materials and methods

Materials and sample preparation

Two commercial available POM copolymers of the same type but different in the stabilising system were used: one type was solely heat stabilised (Ultraform® W2320 003) while the other was additional UV-stabilised (Ultraform® W2320 U03). Commonly used stabilising systems for POM including e.g. phenolic antioxidants and hindered amine (light) stabilisers (HA(L)S) with regard to the final application are described in [5, 6]. Specimens in term of loudspeaker

grills were made by injection moulding. Coloured specimens were obtained by adding a grey master batch on POM substrate in an amount of 3% by mass to the pellets during processing. The master batch is commercially distributed and is used e.g. for the coloration of automotive parts for indoor application. The pigment mixture for the master batch consisted of C.I. Pigment White 6, C.I. Pigment Red 101, C.I. Pigment Brown 24 and C.I. Pigment Black 7 dispersed in POM. Since no further information about the composition of the master batch was available a preliminary thermogravimetric analysis (TGA) was made: the master batch consisted of about 65% by mass of polymer (POM) and organic compounds and about 35% of inorganic material. Differential Scanning Calorimetry (DSC) revealed that the POM substrate belongs to the copolymer group. Samples were designated as GB1-1F0 for the non-coloured just heat stabilised grills, as GB1-1F3 for the coloured just heat stabilised grills, as GB3-1F0 for the non-coloured heat and UV-stabilised grills and finally GB3-1F3 for the coloured heat and UV-stabilised grills.

Artificial thermooxidative ageing was realised by storing the grills at 140 °C in an oven as described for the ageing procedure of POM samples at the laboratory of Ciba-Geigy in [7]. The storage period covered a duration up to 8 weeks. Three grills of each condition were weight by means of an analytical balance prior to the oven storage. The oven ageing was shortly interrupted after 2, 3 and 5 weeks for weighing the grills to follow the evolution of the mass during the exposure to thermooxidation.

Colour measurements

Colour measurements were carried out according the L*,a*,b*-System (CIE-LAB 1976) with a Datacolor MICROFLASH 200. The L*-value indicates the brightness (L* = 0 means black and L* = 100 white), the a*-value the fraction of red respective green and the b*-value the fraction of yellow respective blue in the sample's colour.

Melt volume rate

For the determination of the melt volume rate (MVR) according to EN ISO 1133 the grills were ground (size about 5 mm) and the sample grinding stock was put into the heated tube of the ZWICK 4105.01/03 tester afterwards. The molten material was pressed through a defined orifice under the following conditions T = 190 °C in combination with a load of 2.16 kg.

Thermal analysis

DSC measurements were made with a MDSC 2920 (TA Instruments) by using covered aluminium crucibles containing about 10 mg sample material. The atmosphere was nitrogen with a purge rate of 50.10^3 mm^3/min, the temperature program consisted of two consecutive heating runs with 10 K/min from 30 to 210 °C with a cooling sequence with a rate of also 10 K/min between. The peak maximum temperature (T_p) of each run was determined, since the melting temperature of a polymer is usually considered to correspond with the endothermic maximum [8].

TGA was carried out with a TGA 2050 (TA Instruments). The experimental conditions were: purge gas flow 90.10^3 mm^3/min nitrogen or pressurised air, ceramic sample pan and a heating rate of 10 K/min up to 500 °C. The tangent method recommended in TGA standards for the onset determination (extrapolated onset temperature, T_e) leaded to incomparable results due to different degrees of degradation. Thus for comparison purposes the onset temperature was defined as the temperature at which a mass loss of 3% referring to the initial sample mass was reached [9], it is denoted by $T_{0.03}$ in the following. The TGA furnace outlet was coupled to a Quadrupole Mass Spectrometer (QMS) (Thermostar, Balzers) by a heated quartz capillary tube (120 °C) to follow evolved gases during material degradation. A scan was taken every 10 K temperature increase in a range of 1–120 amu with a resolution of 1 amu.

Mechanical testing

Mechanical testing was carried out to determine the resistance against impression stress. For that a self-made equipment (Fig. 1) consisting of a bearing ring of 90 mm inside diameter and a cylindrical loading nose with a spherical end (radius 10 mm) which were mounted in a universal testing machine (Zwick Z050) was used. The concave loudspeaker grills were put approximately central on the bearing ring with the outside side down and a force was exercised with the loading nose in the middle of the inner surface until a break failure occurred. The rate of the crosshead motion was 20 mm/min. The force and the displacement were registered during the experiment. Typically, 10 grills were tested for the initial condition while the sample size was reduced to 3 for the thermooxidative aged grills due to the limited space in the oven.
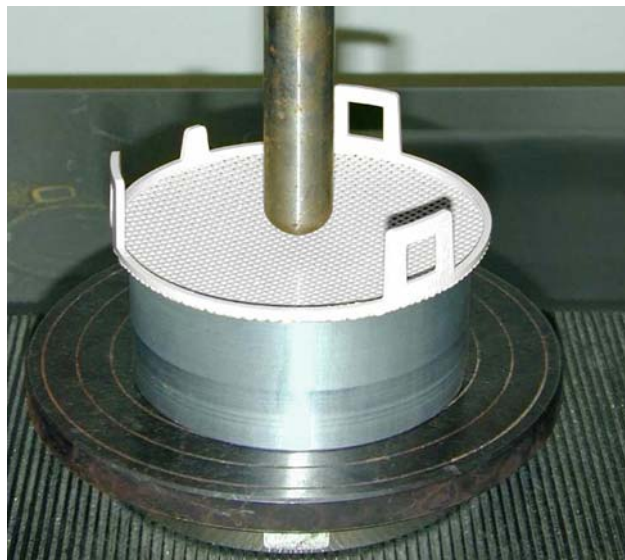

Fig. 1 Perforation test device

Results and discussion

After the artificial ageing the surface of non-coloured samples showed visible changes in comparison with the initial condition: specimens were discoloured and exhibited a yellowing. For coloured specimens no change of the sample surface could be observed at the first look.

The average mass loss during the storage at 140 °C was highest for GB3-1F3 with about 5% after 8 weeks followed by GB1-1F3 and GB3-1F0 (about 4%), while it was lower than 2% for GB1-1F0 (Table 1). It can be presumed that the addition of the colorant enhanced the influence of the thermooxidative degradation with the result of an increase in the mass loss during oven ageing in comparison with the non-coloured grills of the same condition.

Colour measurements

The colour measurement (Table 2) showed for the both non-coloured materials that there was a slight difference in the colour which was not visible with the naked eye. The L*-value of GB1-1F0 was found two units whiter than for GB3-1F0. The addition of colorant increased in every case the L*-value of at least one unit. The a*-value of GB3-1F0 indicated a higher amount of green in comparison with GB1-1F0, while the coloration reduced the green amount in the heat and UV-stabilised material, there was no detectable effect on the solely heat stabilised material. The b*-value showed a similar slight blue tint for the

Table 1 Mass loss (%) in dependence of the oven storage duration at 140 °C [mean (*x*) and standard deviation (*s*) of three measurements]

Duration (weeks)	GB1-1F0		GB1-1F3		GB3-1F0		GB3-1F3	
	x	*s*	*x*	*s*	*x*	*s*	*x*	*s*
2	0.1	0.06	0.9	0.03	0.3	0.01	1.1	0.06
3	0.5	0.03	1.3	0.07	0.9	0.05	1.6	0.11
5	0.9	0.01	2.4	0.29	2.2	0.06	3.0	0.21
6	1.0	0.02	3.0	0.31	2.5	0.07	3.7	0.27
7	1.2	0.02	3.7	0.39	3.1	0.09	4.4	0.37
8	1.5	0.02	4.4	0.49	4.1	0.09	5.3	0.49

non-coloured materials and a similar slight yellow tint for both materials after coloration.

Oven aged non-coloured just heat stabilised specimens turned visibly into yellow with the duration of the storage but the degree of discoloration was not so intensive as for the heat and UV-stabilised non-coloured specimens. Yellowing is often associated with formation of double bonds and other chromophoric structures in the polymer chain during ageing. In the case of POM discoloration results apparently from the deterioration of the added stabilising system as discoloured material became white again after additive extraction by dissolution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 40 °C and precipitation in a solution of toluene as described by Hasegawa [10]. In [5, 6, 11] it is reported that stabiliser like phenolic antioxidants cause discoloration when they are consumed as radical scavenger, but stabilisers on the basis of amines are also known to lead to discoloration [6]. From this it follows that the discoloration of the non-coloured grills can be considered as an indicator of the stabiliser consumption. Colour measurements of the coloured samples confirmed the first look impression that there

Table 2 Colour measurements according to the LAB-system [mean (*x*) and standard deviation (*s*) for 10 measurements]

Sample + treatment	*L**-value		*a**-value		*b**-value	
	x	*s*	*x*	*s*	*x*	*s*
GB1-1F0	72.9	0.4	–0.74	0.06	–4.54	0.17
GB1-1F0 3 W 140 °C[a]	78.3	0.5	–1.63	0.08	2.92	0.56
GB1-1F0 5 W 140 °C	77.3	0.7	–1.93	0.08	3.74	0.42
GB1-1F3	74.2	0.1	–0.57	0.01	2.16	0.06
GB1-1F3 3 W 140 °C	74.0	0.1	–0.71	0.01	2.82	0.07
GB1-1F3 5 W 140 °C	74.1	0.1	–0.74	0.01	3.12	0.13
GB3-1F0	70.9	0.1	–1.44	0.02	–3.93	0.02
GB3-1F0 3 W 140 °C	72.0	0.2	–2.20	1.74	8.99	0.74
GB3-1F0 5 W 140 °C	71.8	0.1	–3.02	0.05	12.24	0.28
GB3-1F3	74.2	0.0	–0.63	0.01	2.09	0.01
GB3-1F3 3 W 140 °C	73.9	0.1	–0.81	0.02	4.01	0.17
GB3-1F3 5 W 140 °C	73.8	0.0	–0.90	0.01	4.57	0.06

[a] Weeks at 140 °C abbreviated W 140 °C

was no real change in the colour after the oven ageing. So the colorant restrains or even compensates the discoloration effects of the stabilisers.

MVR

The coloration shows no remarkable effect on the initial condition MVR values, all measured MVRs were within a range of three units. The thermooxidative ageing leaded in every case to an increase in the MVR. The increment was clearly higher for the material containing an additional UV-stabiliser in comparison with the solely heat stabilised material. Furthermore the GB3-1F3 sample showed the highest increase after 5 weeks oven storage. For the non-coloured and coloured grills a correlation between the increase in the MVR and the *b**-value of the colour measurement could be found (Fig. 2). As the MVR is commonly coherent with the average molar mass a change in the MVR value can be referred to changes in the molecular structure through e.g. crosslinking (decrease) or chain scission (increase) [12]. Thus, one can assume that chain scission leading to a reduction of the molar mass occurred during ageing. Previous investigations on POM-C injection moulded specimens were carried out by means of high temperature gel permeation chromatography (GPC) measurements in dimethylformamide (DMF) at 140 °C on the initial condition and on samples stored 3 weeks at 140 °C. As one can see in Fig. 3 some slight degradation can be detected for the UV-stabilised copolymer after oven storage. For the solely heat stabilised material the M_n (number average), the M_w (weight average) and the curve shape revealed no significant differences. Similar results with negligible differences between original and aged material in the case of GPC investigations were obtained by Showaib and Wyzgoski [13].

As reported by several authors [1, 14–16] thermooxidative ageing of POM leads in a first step to the formation of hydroperoxide groups in the macromolecular chain. Additional thermal treatment induces finally a β-chain scission in the acetal-linkage near the hydroperoxide subtituent. So the explanation for the contradictory results in MVR and GPC measurement could be the following: During ageing hydroperoxides are formed in terms of a predamage in the polymer chain without inducing chain scission. For the GPC measurements the used temperature is high enough for the dissolution of the polymer but not high enough to initiate the chain scission as additional the solvent contains a stabiliser to hinder degradation during sample analysis. So the molar mass is not affected as the chain backbone remains intact and the hydroperoxide
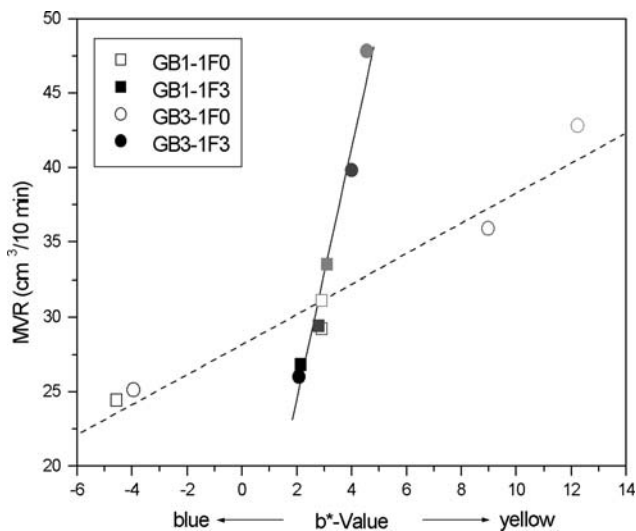
Fig. 2 Correlation between the MVR and the b^*-value of the colour measurements. *Black symbols* initial condition, *grey symbols* after 3 weeks at 140 °C and *light grey symbols* after 5 weeks at 140 °C

substituents are to small in comparison with the complete chain to bring out a remarkable change in the molar mass. The temperature of the MVR-measurements is above the melting temperature of the POM material and above the range reported for the occurrence of themooxidative degradation. As the presence of oxygen in the MVR device is limited no additional peroxide substituents will be generated, but those already existing in the thermooxidative aged material in combination with mechanical shear forces and heat are leading to the β-scission in the macromolecular
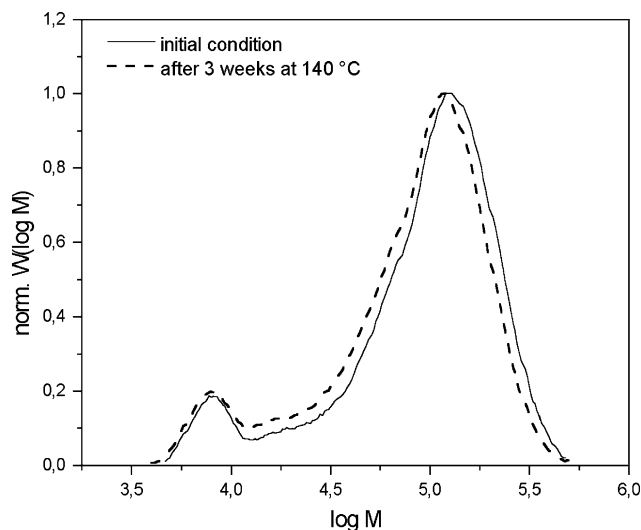

Fig. 3 Influence of ageing on the molar mass distribution of the heat and UV stabilised copolymer (*non-coloured*)

chains. The accelerated chain scission can be observed through a molar mass reduction resulting in an increase in the MVR-value. It follows that both of the methods reveal that the non-coloured additional UV-stabilised material is more affected through oven ageing than the solely heat stabilised one.

DSC

Since thermal treatment at 140 °C changes the thermal history of the material through annealing in the following only the results of the cooling sequence and the second heating run will be considered to discuss the influence of coloration on ageing. The presented data are mean values of 2–4 measurements. The observed maximum range of the peak temperature (T_p) for four measurements of a sample was 3 K. T_p of the melting curve occurred at 170 °C for the sample taken from GB1-1F0 at the initial condition. After 5 weeks oven storage at 140 °C neither a change in T_p nor in the shape of the melting curve could be observed. For the sample taken from the grill GB1-1F3 the initial T_p of 168 °C was not affected by the 5 weeks oven storage period, again the change in the melting curve shape was negligible. Material taken from grills GB3-1F0 and GB3-1F3 showed for both of the samples a T_p of 169 °C at the initial condition. The average T_p shifted to 168 °C after the oven storage duration of 5 weeks. Once more no difference in the profile of the melting curves could be detected.

Since the pigments constitute additional nucleation centres one would expect an increase in the crystallisation rate and therefore a change in the crystallisation behaviour of the coloured samples. However, no change during the cooling sequence could be noticed in the DSC curves either with regard to coloration or with regard to ageing as the differences observed in the T_p ranged within the standard deviation of about 1 K.

TGA/MS

The onset temperature ($T_{0.03}$) for the used grey master batch determined at the beginning of the experiment series was 255 °C in air atmosphere and 275 °C in nitrogen. In both atmospheres the $T_{0.03}$ was found to be at least 10 °C lower than the $T_{0.03}$ of the two non-coloured materials. However the measurements in nitrogen of GB1-1F0 and GB1-1F3 (Fig. 4a) did not differ in their TG (thermogravimetric) and DTG (derivative TG) curve profile—both of the samples showed a one step degradation—either at the initial condition or after the 5 weeks storage at 140 °C. So in
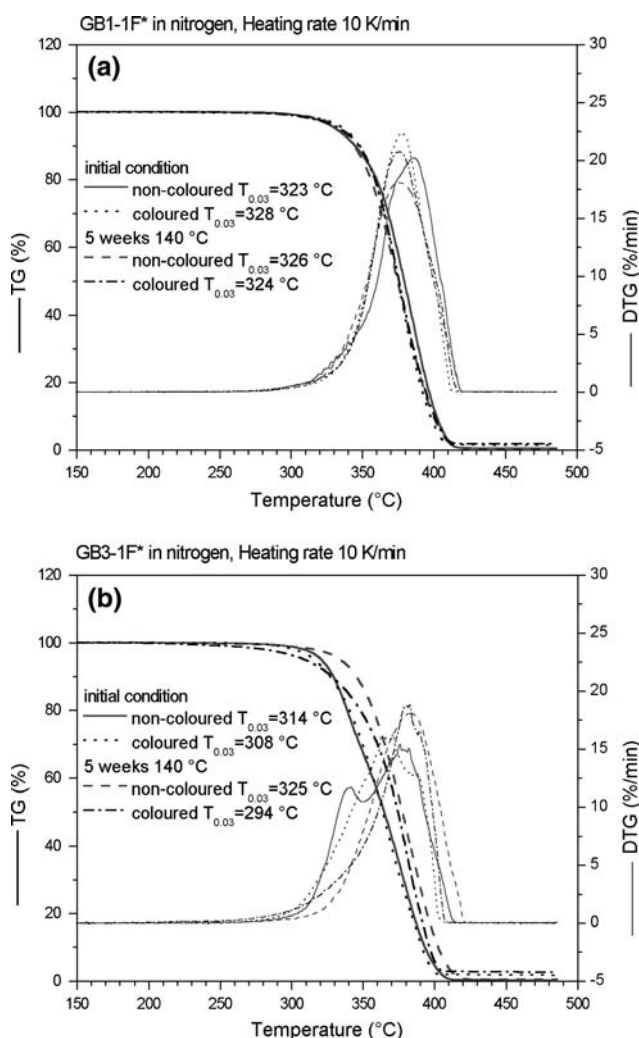
Fig. 4 TGA in nitrogen in dependence of the oven storage duration: (a) heat stabilised copolymer, (b) heat and UV-stabilised copolymer

of the $T_{0.03}$ some molecular chain reorganisations can be noticed [9].

The accompanying MS-measurements show that the main degradation product is formaldehyde (m/z 30) but there are also some fragments belonging to trioxane (m/z 31, 61, 89) that can be detected in a reduced scale. Also in a reduced scale fragments that can be assigned to the comonomer (m/z 43, 45, 60), the stabilising system (m/z 57 and m/z 77 from hindered phenols) and carbon dioxide (m/z 44) can be found (Fig. 5). It should be mentioned that in the MS additional ion fragments were detected but no attempt was made to identify all of the compounds. According to [17] they should consist of low molar mass methoxy oligomers and 1,3,5-trioxanes with methoxy substituents. The evolution profiles of GB3-1F3 at the initial condition (Fig. 5a) and after an ageing period of 5 weeks at 140 °C (Fig. 5b) show that the peak maxima
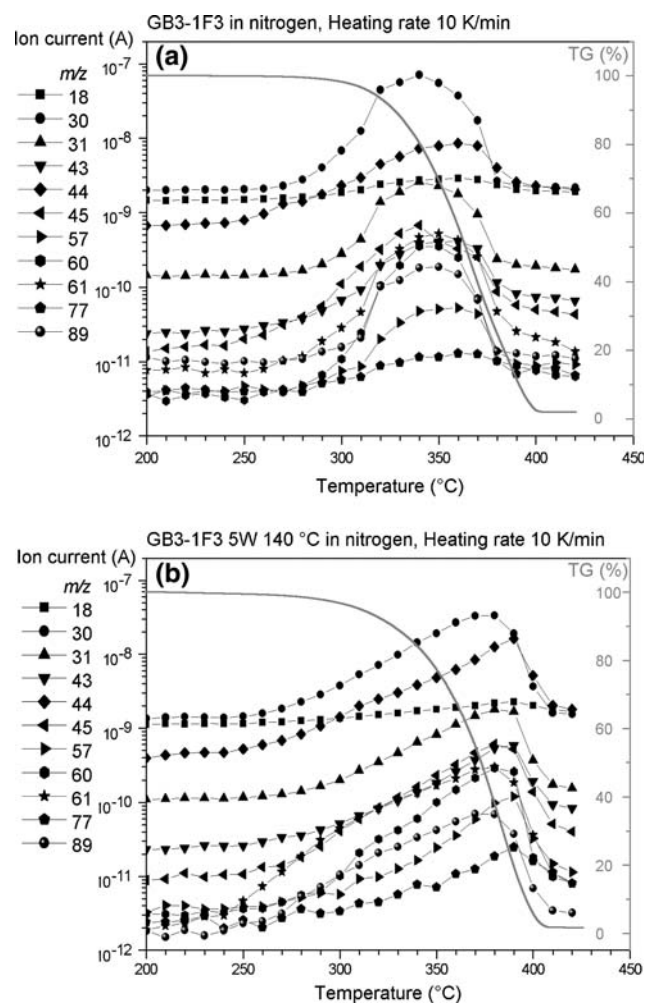

Fig. 5 TGA-MS in nitrogen, coloured heat and UV-stabilised copolymer: (a) initial condition, (b) after 5 weeks at 140 °C
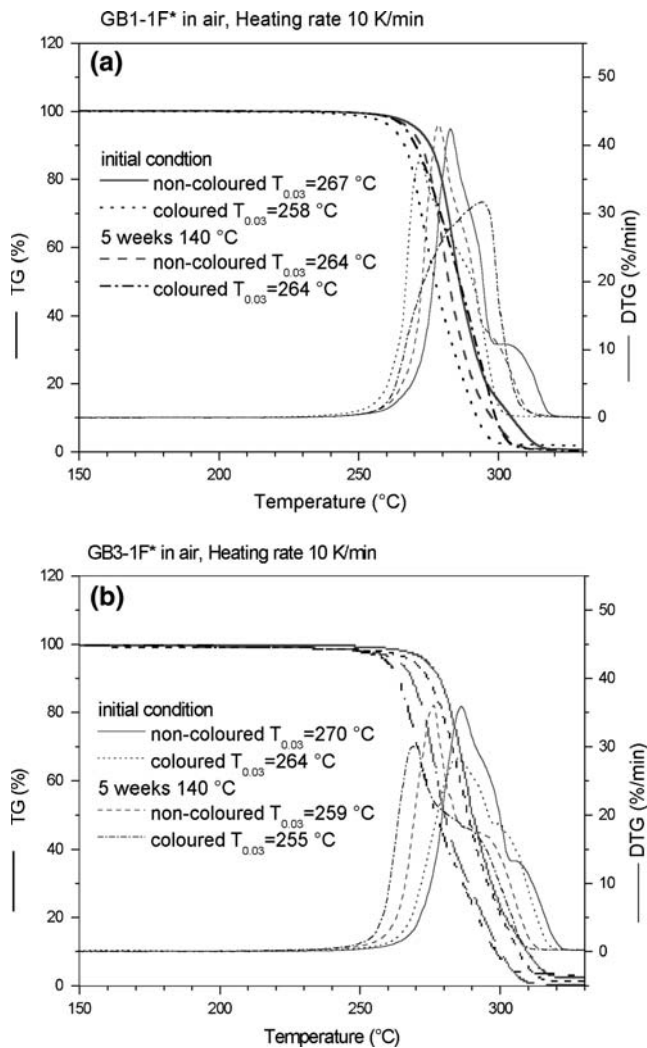
the case of the solely heat stabilised material no influence of the coloration emerged. On the other hand the measurements of GB3-1F0 and GB3-1F3 (Fig. 4b) revealed differences in the degradation behaviour at the initial condition. Even the differences in the TG curves of GB3-1F0 and GB3-1F3 were not clearly apparent at the first look—both samples seemed to show a one step degradation—the DTG curves where not similar. The DTG of GB3-1F0 had two peaks: one smaller peak occurring at about 340 °C and one major peak at about 380 °C, which corresponds to the DTG peak maximum of the other investigated materials. After a storage period of 5 weeks at 140 °C the bimodal profile of the DTG curve changed to a single peak and the small peak was no longer existent. With respect to the DTG peak change and the clear decrease

Fig. 6 TGA in air in dependence of the oven storage duration: (**a**) heat stabilised copolymer, (**b**) heat and UV-stabilised copolymer

of the released degradation products are shifted to a higher temperature range. This is consistent with the observed change in the corresponding DTG curves.

The TG profiles in air (Fig. 6) of the samples without colouring showed no longer a clear one step degradation. Above a temperature of about 290 °C the degradation rate became remarkably slower, resulting in a decrease in the inclination of the TG curve and the appearance of a shoulder in the DTG curve. The existence of a thermal stable part in the thermal degradation of POM-diol and its formation mechanism has been reported by several authors [18–20]. The TGA measurements showed that the addition of a colorant had an influence on the thermooxidative degradation since the $T_{0.03}$ of the coloured grills was lower than that of the non-col-

oured ones. After the oven ageing of 5 weeks at 140 °C different results were observed in dependence of the coloured grill's stabilising system. While the samples taken from GB3-1F3 showed a shift to lower temperature in the course of the TG curve in comparison with the initial state, the samples from GB1-1F3 had a TG profile that was shifted to higher temperature than that of the initial state. For the non-coloured materials the TG curves were shifted to lower temperature after ageing. The shift was found to be stronger for the heat and UV-stabilised material in comparison with the solely heat stabilised material.

In air the corresponding MS spectra showed that the main degradation products are formaldehyde again and carbon dioxide but in the presence of oxygen additional formation of water (m/z 18) took place (Fig. 7). Several other compounds as mentioned above were detected too. The comparison of the evolution profile of the initial condition of GB3-1F3 (Fig. 7a) with that of the aged one (Fig. 7b) revealed that the slope of the evolved gases in the temperature range from 250 to 270 °C is more pronounced for the aged condition. This is due to the earlier begin of the thermooxidative degradation as can be seen on the corresponding onset temperature in the TG profile. In the considered temperature range the degradation of the aged sample is progressed and this leads to a higher release of volatile compounds.

Mechanical testing

The influence of thermooxidative ageing at elevated temperature on the mechanical properties in term of resistance against perforation stress is summarised in Table 3. The average of the force maximum of the non-coloured material increased after 3 weeks oven storage before it regained the value of the initial condition after 5 weeks oven storage, but the observed differences were in the range of the standard deviation. The force maximum of the coloured material was higher compared to that one of the non-coloured material. In the case of aged material the value became lower in dependence of the oven storage duration. Even the initial force maximum values of both coloured samples (GB1-1F3 and GB3-1F3) were nearly the same, they differed remarkably after the oven storage. The GB3-1F3 grill lost more of its initial force maximum value already after 3 weeks oven storage than the GB1-1F3 grill after 5 weeks oven storage.

A correlation between the displacement at break and the b^*-value could be found for the coloured grills as can be seen in Fig. 8.
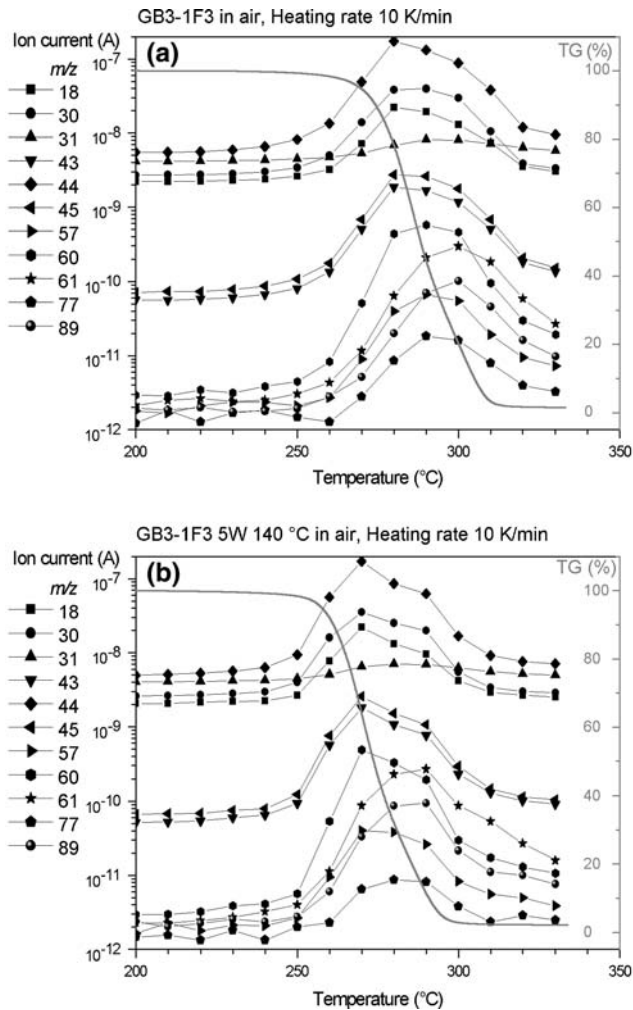
GB3-1F3 in air, Heating rate 10 K/min

GB3-1F3 5W 140 °C in air, Heating rate 10 K/min

Fig. 7 TGA-MS in air, coloured heat and UV-stabilised copolymer: (**a**) initial condition, (**b**) after 5 weeks at 140 °C

Table 3 Impression resistance test: force maximum (F_M) and displacement (d) at break [mean (x) and standard deviation (s) for three (ten initial condition) measurements]

Sample + treatment	F_M (N)		d (mm)	
	x	s	x	s
GB1-1F0	143	32	5.7	0.7
GB1-1F0 3 W 140 °C	166	31	6.1	0.7
GB1-1F0 5 W 140 °C	151	28	5.9	0.6
GB1-1F3	216	24	7.3	0.5
GB1-1F3 3 W 140 °C	203	34	7.0	0.7
GB1-1F3 5 W 140 °C	168	18	6.2	0.4
GB3-1F0	216	21	7.2	0.5
GB3-1F0 3 W 140 °C	174	24	6.5	0.5
GB3-1F0 5 W 140 °C	149	20	5.9	0.4
GB3-1F3	222	31	7.4	0.7
GB3-1F3 3 W 140 °C	165	25	6.1	0.4
GB3-1F3 5 W 140 °C	139	25	5.5	0.6

to thermooxidative influence as the mass loss is enhanced. MVR, TGA and mechanical test results show that depending on the stabiliser package the effects of coloration are different. The solely heat stabilised material is less sensitive to thermooxidative ageing at elevated temperature than the heat and UV-stabilised material, this tendency is persistent even after coloration. After ageing the coloured heat and UV-stabilised material loses more of its initial properties in comparison with the non-coloured material. This is particularly true for the MVR and the mechanical testing results. Finally, for the coloured grills a correlation between the evolution of the discoloration and the change in mechanical properties as well as between the discoloration and the MVR results can be established.
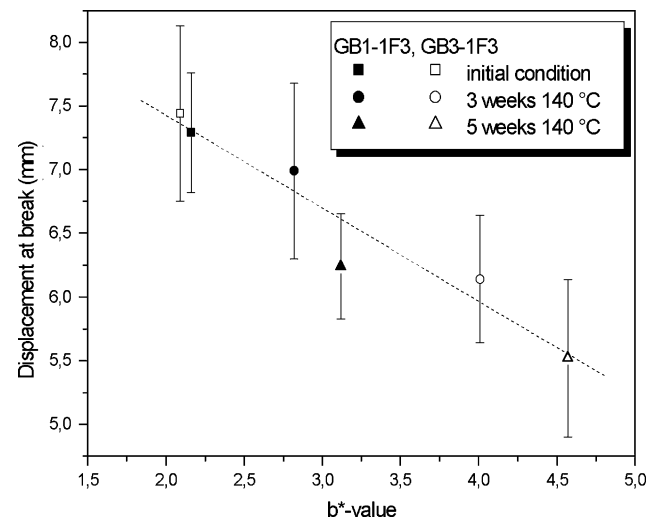
Summary and conclusions

Thermooxidative ageing of non-coloured POM equipped with a stabiliser package leads to discoloration due to the consumption of the active sites in the antioxidants. The discoloration, which depends on the exposure duration, can be restrained by the use of a colorant. The addition of the colouring master batch does not affect the melting behaviour of the POM material as differences in the DSC and MVR results are negligible. Also the non-isothermal crystallisation behaviour shows no change in the profile of the DSC curve during the cooling sequence, even one would have expected a faster crystallisation because of the additional nucleating centres in terms of the pigments. The use of the colorant is beneficial in the case of hindering discoloration during ageing but on the other hand one has to take into account a higher sensitivity

Fig. 8 Correlation between the displacement at break of the perforation tests and the b^*-value of the *colour* measurements

References

1. Kern W, Cherdron H, Jaacks V (1961) Die Angew Chem 73:177
2. Weissermel K, Fischer E, Gutweiler K, Hermann HD (1964) Kunststoffe 54:410
3. Masamoto J (1993) Prog Polym Sci 18:1
4. Noatsch M, Reuter F (2001) Kunststoffe 91:296
5. Sabel HD, Schlaft H, Unger P, Ziegler U (1992) In: Bottenbruch L (ed) Technische Thermoplaste: Polycarbonate, Polyacetale, Polyester, Celluloseester. Kunststoff-Handbuch 3. Carl Hanser Verlag, Munich, Vienna, p 300
6. Zweifel H (2000) Plastic additives handbook, 5th edn. Carl Hanser Verlag, Munich, Vienna, p 11, 86
7. Stohler FR, Berger K (1990) Angew Makromol Chem 176/177:323
8. Grellmann W, Seidler S (2005) Kunststoffprüfung. Carl Hanser Verlag, Munich, Vienna, p 308
9. Archodoulaki VM, Lüftl S, Seidler S (2004) Polym Degrad Stab 86:75
10. Hasegawa S, Takeshita H, Yoshii F, Sasaki T, Makuuchi K, Nishimoto S (2000) Polymer 41:111
11. Epacher E, Fekete E, Gahleitner M, Pukánsky B (1999) Polym Degrad Stab 63:489
12. Ehrenstein GW, Kuhmann K (1993) Recycling von Thermoplasten, Literaturrecherche (edited by Süddeutsches Kunststoffzentrum, Würzburg)
13. Schowaib EA, Wyzgoski MG (2002) J Mater Sci 37:1895
14. Blyumenfeld AB, Neiman MB, Kovarskaya MB (1966) Vysokomol Soed 8:1990
15. Sedlář J, Kučera M (1967) Makromol Chem 102:245
16. Kern W (1967) Chemiker Ztg/Chem Apparatur 91:255
17. Day M, Cooney JD, Touchette-Barrette C, Sheehan SE (1999) J Anal Appl Pyrolysis 52:199
18. Dudina LA, Enikolopyan NS (1963) Vysokomol Soed 5:1135
19. Jaacks V (1966) Macromol Chem 99:300
20. Blyumenfeld AB, Kotrelev MV, Kovarskaya BM (1970) Vysokomol Soed A 12:81