Degradation Behavior of Polyoxymethylene: Influence of Different Stabilizer Packages

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ABSTRACT: Stabilizer effects of two types (homopolymer and copolymer) of commercially available polyoxymethylenes containing two different stabilizer packages under various aging conditions have been studied by the application of thermogravimetric analysis coupled with mass spectrometry. Increasing yellowness during thermooxidative aging has been observed. Investigations of the melt volume rate have proved that the UV-stabilized materials exhibit a higher increase in the melt volume rate after oven aging, which is caused by reactions of the additives, than the solely heat-stabilized materials. The thermogravimetric analysis/mass spectrometry investigations have proved broad synergy effects between the heat- and UV-stabilizer systems. The formation of chains with thermally stable end groups or of cyclic products proceeds during aging, particularly in the presence of UV stabilizers. This formation might be the result of intermolecular transacetalization reactions. The degradation behavior of UV-irradiated homopolymer and copolymer samples has also been investigated. Oven storage and weathering cause comparable shifts in the derivative thermogravimetry traces, so similar damage reactions can be suggested. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3679–3688, 2007

Key words: ageing; degradation; irradiation; stabilization; thermogravimetric analysis (TGA)

INTRODUCTION

Polyoxymethylene (POM), also known as acetal or polyacetal, is a highly crystalline high-performance engineering thermoplastic polymer that displays a broad range of properties; among the most notable are its low coefficient of friction, excellent wear resistance, high modulus, and resistance to many solvents and automotive fuels. The mechanical properties include high strength and stiffness coupled with good impact strength. Because of their practical application, polyacetals are stabilized against oxidation and other environmental influences such as UV irradiation.

In a previous article,[1] the authors reported the degradation and stabilizer consumption of commercially available heat-stabilized POM homopolymer and copolymers. Thermogravimetric analysis (TGA) indicated random scission of the polymer chain as the initiation mechanism of the degradation of POM. The observed depression in the onset temperature of the thermogravimetry (TG) curves, dependent on the duration of the artificial aging, was a result of continuous stabilizer consumption.

This article deals with the degradation and stabilizer consumption of a POM homopolymer and a POM copolymer, which contain stabilizer packages against heat as well as heat and UV loading. Because of the expected degradation mechanism, different stabilizers have been used for POM:[2–4]

- Suppressing autoxidative degradation reactions can be achieved with antioxidants, such as sterically hindered phenols.
- Degradation by secondary products of oxidation can be prevented by the addition of stabilizing agents such as acid acceptors or other products reacting with free formaldehyde.
- Degradation through acidolysis and hydrolysis can be inhibited through
  1. Capping of the end groups by esterification or etherification.
  2. Copolymerization.
  3. Addition of antioxidants, formaldehyde scavengers, and other stabilizers.
- To improve the light stability, the best results are obtained by a combination of a sterically hindered amine light stabiliser (HALS) and UV absorber.

EXPERIMENTAL

Materials and aging procedure

Commercial heat-stabilized and heat- and UV-stabilized homopolymers and copolymers were supplied by DuPont (Wilmington, DE) and BASF (Ludwig-

TABLE I
Investigated Materials and Conditions

	Material			
	Homopolymer		Copolymer	
Condition	Heat-stabilized	Heat- and UV-stabilized	Heat-stabilized	Heat- and UV-stabilized
As-received (pellet)	Heat-stabilized	Heat- and UV-stabilized	Heat-stabilized	Heat- and UV-stabilized
Injection-molded specimen	H11	H21	C11	C21
Injection-molded specimen, oven-aged	H11.56d/140°C	H21.56d/140°C	C11.56d/140°C	C21.56d/140°C
Injection-molded specimen, xenon-tested[a]	H11 1a Xe	H21 2a Xe	C11 1a Xe	C21 2a Xe

[a] 1 and 2 years of car–indoor application.

shafen, Germany). Injection-molding grades with a high flow [melt volume rate (MVR) at 190°C $\approx$ 20 cm^3/10 min] were used. No further information about the stabilizer package was given for proprietary reasons. However, adequate stabilizer packages are given in refs. 2–4, such as UV absorbers of the 2-hydroxybenzophenone type and HALS for UV stabilization, whereas Irganox 245 has been reported to be the best antioxidant. The color of the resins was whitish because no colorants were added. Specimens with a length of 145 mm, a width of about 10 mm, and a thickness of 4 mm according to ISO 3167 were prepared by injection molding. To study the stabilizer effectiveness, suitable volumes of the received POM pellets were purified, as described by Hasegawa et al.,[5] to remove stabilizers and other additives.

The two POM materials were subjected to accelerated aging to induce stabilizer consumption. The thermal aging was performed at 140°C (maximum temperature deviation: 1.5°C) in an oven (Heraeus) for 21, 35, and 56 days. In Table I, the abbreviations for the samples are listed with respect to the aging procedure.

To clarify if the observed discoloration was provoked by a chemical reaction of the stabilizers or as a result of the formation of chromophore groups [e.g., double bonds in degraded poly(vinyl chloride)], aged pellets were purified after the aging procedure too.

For UV irradiation, an artificial weathering test using a xenon tester (Suntest XLS+, Atlas, Germany) was carried out. This test simulated the standard climate conditions of car–indoor irradiation for Central Europe (irradiation dose equivalent for 1 year = 1709 MJ/m^2, black panel temperature $\sim$ 50°C). The xenon tests simulated 1 and 2 years of car–indoor UV irradiation (Table I).

Degradation analysis

For TGA performed with a TA Instruments (Delaware, USA) TGA 2050, samples of about 10 mg were heated in air and nitrogen atmospheres with a purge gas stream of 100 mL/min in ceramic pans at a heating rate of 10 K/min. The onset temperature, that is, the temperature at which the degradation started, was defined by a mass loss of 3% with respect to the initial sample mass because the commonly used tangent method gives irreproducible results.[1,6]

Coupling with mass spectrometry (MS) enabled a simultaneous analysis of specific degradation products that evolved during thermal degradation. Gases evolving during the decomposition of the sample were registered after every 10°C step of the temperature increase. The mass spectrometer was a Thermostar (Balzers, Liechtenstein). The coupling consisted of a heated quartz capillary tube (120°C) connecting the TGA furnace outlet to the MS gas inlet through a pinhole diaphragm.

Fourier transform infrared spectrometry was carried out with a Tensor 27 (Brucker Optics, Germany) equipped with a diamond attenuated total reflection unit (DuraSamplIR II). The scanned wave-number range was 4000–600 cm^{-1}, with a resolution of 2 cm^{-1}. The POM pellets and the purified powder were melted to a bulk and cooled under a nitrogen atmosphere in a differential scanning calorimeter at 10 K/min to obtain similar surfaces for the samples because the signal intensity of the attenuated total reflection/Fourier transform infrared depended on the sample's surface roughness.

The molar mass investigations were conducted by means of gel permeation chromatography (GPC). The investigations were performed at an elevated temperature (140°C) with a PL-GPC 220 instrument (Polymer Laboratories, Amherst, MA) equipped with two separation columns and a differential refractometer. N,N-Dimethylformamide was used as an eluent at a flow rate of 0.5 mL/min. The calibration was made with polystyrene standards.

The MVR investigations were performed according to ref. 7 (applied mass = 2.16 kg, cylinder temperature = 190°C). To assess the yellowing progress, b* according to the CIELAB method[8] was determined. (CIE 1976 (/L*/, /a*/, /b*/) color space* (also called CIELAB, with coordinates /L*/, /a*/, and /b*, *L*/for luminance and */a/* and */b/* for the color-opponent dimensions)).
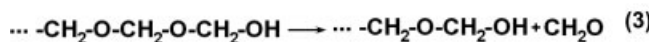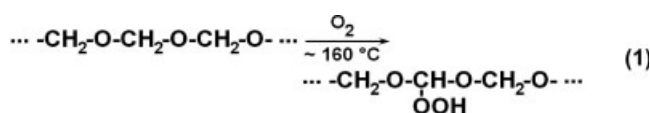
RESULTS AND DISCUSSION

As the degradation of POM mainly involves a zipper mechanism, TGA investigations are adequate to

TABLE II
Measurements of b^* Under the Initial Condition and
After 21 days of Oven Aging

Specimen	b^*	
	Initial condition	21 days at 140°C
H11	−2.8	9.1
H21	−2.0	11.8
C11	−4.5	7.8
C21	−3.7	10.8

TABLE III
Mass Loss with Respect to the Storage Duration

		Mass loss after 35 days at 140°C (%)	Mass loss after 56 days at 140°C (%)
Pellet	H1	2.3	7.5
	H2	7.7	18.5
	C1	1.3	3.1
	C2	1.9	4.1
Specimen	H11	2.6	5.4
	H21	3.6	8.9
	C11	1.2	2.5
	C21	1.6	3.2

determine the relative stability of different stabilized polyacetals. The TGA investigations, as reported in ref. 1, reveal that thermooxidative processes reduce the degradation onset of the homopolymer and copolymer pellets because the secondary products of the autoxidation enhance the autoxidation and/or autocatalytic cleavage of the C—O—C bonds. Random scission of the polymer chains and the formation of macroalkyl radicals, which form alkylperoxyl and hydroperoxides in the presence of even a small amount of oxygen, lead to subsequent degradation. According to ref. 9, oxygen can react with the POM chain, and hydroperoxides are formed according to eq. (1). The hydroperoxides can either initiate chain scission with the succeeding formation of formaldehyde [eq. (3)] or oxidize formaldehyde into formic acid:

$$\cdots -CH_2-O-CH_2-O-CH_2-O- \cdots \xrightarrow[\sim 160\,°C]{O_2} \atop \cdots -CH_2-O-\underset{OOH}{CH}-O-CH_2-O- \cdots \quad (1)$$

$$\cdots -CH_2-O-\underset{OOH}{CH}-O-CH_2-O- \cdots \xrightarrow{thermal} \cdots -CH_2-OH \atop + \text{other products} \quad (2)$$

$$\cdots -CH_2-O-CH_2-O-CH_2-OH \longrightarrow \cdots -CH_2-O-CH_2-OH+CH_2O \quad (3)$$

Copolymerization with some thermally stable monomers (e.g., dioxolane and ethylene oxide) decelerates chain rupture processes because the unzipping reaction is stopped at the first comonomer unit.[10]

During the accelerated aging of UV-stabilized polyacetals at elevated temperatures, yellowing as an additional effect has to be considered. The discoloration of the POM samples after accelerated aging could be detected by the human eye; measurements of the b^* value according to ref. 8 reveal furthermore that all investigated UV-stabilized products are much more inclined to yellowing than solely heat-stabilized materials (Table II).
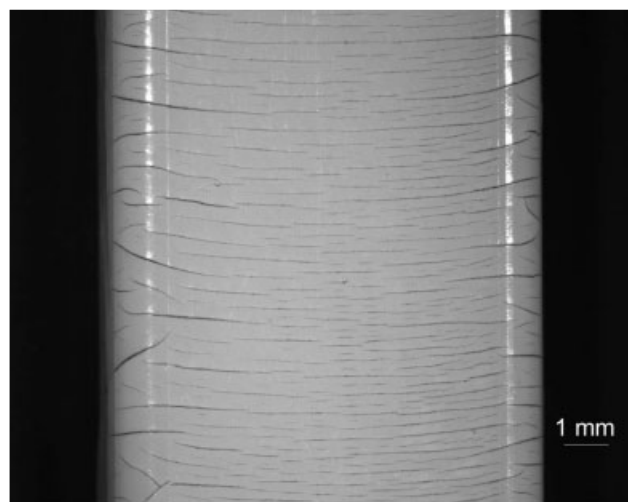
A storage time of 21 days at 140°C leads to visible surface cracks, and after 35 days, the UV-stabilized materials have lost significantly more mass (independent t test, significance level = 0.05) than the

solely heat-stabilized materials (Table III), as simultaneous mass measurements have revealed. The deterioration of the homopolymer (H11) after oven aging and UV irradiation is shown in Figure 1.

It is well accepted that the discoloration of polyacetals after compounding and under service conditions is usually initiated by additives, including antioxidants.[3] After the extraction of the additives, POM

(a)

(b)

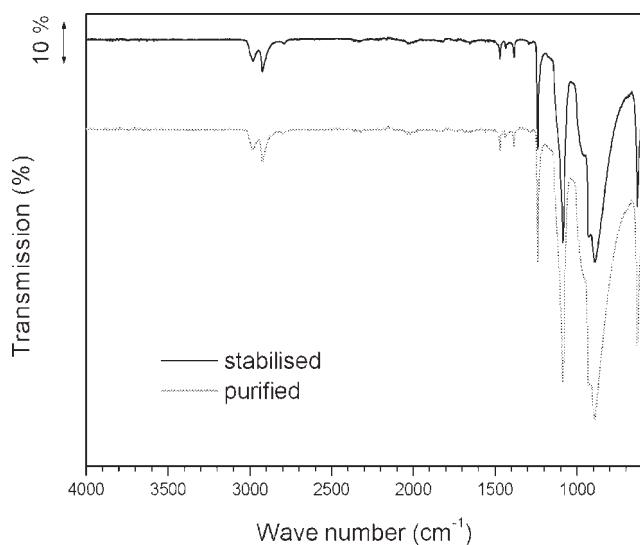**Figure 1** Heat-stabilized homopolymer (H11): (a) after oven aging and (b) after UV irradiation.

Figure 2 IR spectrum of the homopolymer (H1) under the initial condition and after additive purification.

becomes whitish again. This effect leads to the assumption that the discoloration of polyacetals is initiated by additives, not by degradation. The recombination of polyacetal radicals should give a linear chain too without chromophoric groups such as conjugated double bonds.

The IR spectra of the sample under the initial condition and of the additive-purified sample show nearly no changes in the absorption bands (Fig. 2). Only in the area around 1000 cm^{-1} can a higher intensity for the purified pellet be observed because of the different crystallization behaviors of the samples.

Complementary information about viscosity changes after the aging treatment has been obtained with MVR measurements. Those results reveal that during accelerated aging at 140°C, the MVR increases (Table IV). This can be explained in terms of changes in the molecular structure, as an increase in the MVR is an indicator of damage in polymer chains for POM materials too.[11] Table IV further reveals that the changes in the MVR value of the UV-stabilized materials (C21 and H21) are higher than those of the heat-stabilized materials (C11 and H11). This result is consistent with the fact that in the case of extended thermooxidative aging, decomposition of the UV stabilizers comes first. The stabilizer molecules can take part in various transformation reactions; for example, conjugated dienones can be formed. The formation of these compounds leads to the discoloration of the polymer, and small changes in the molecular structure result in chain damage as a further implication. Thus, the measured values of the MVR are higher (e.g., the viscosity is lower), and it can be deduced that chain damage occurs. When the storage time at 140°C is increased, the UV-stabilized POM materials tend to degrade to a higher extent than the solely heat-stabilized materials.

TABLE IV
MVR Investigations Under the Initial Condition and After 21 and 35 Days of Oven Aging

Specimen	Initial condition (cm$^3 \times 10$/min)	21 days at 140°C (cm$^3 \times 10$/min)	35 days at 140°C (cm$^3 \times 10$/min)
H11	21.0	23.9	—
H21	21.3	26.9	—
C11	26.6	30.7	37.4
C21	24.8	32.4	43.1

To verify the hypothesis concerning the stabilizer effect, TGA investigations in an air atmosphere have been performed (illustrated in Figures 3–5).

In Figure 3, the TGA results reveal that in contrast to the findings of the heat-stabilized products reported in ref. 1, the investigated heat- and UV-stabilized homopolymers are nearly as stable as the copolymers. In ref. 1, the reported onset temperatures for the heat-stabilized polymers are 246°C for the homopolymer pellet and 258°C for the copolymer pellet. As for Figure 3, the measured onset temperatures for the heat- and UV-stabilized homopolymer and copolymer pellets are 264 and 262°C, respectively.

Comparing the results presented for the pellets (Fig. 3) and for the injection-molded samples (Fig. 4), we can observe the influence of processing: although the onset temperature of the homopolymer decreases from the pellet to the specimen condition (H21: onset temperature = 247°C), the copolymer remains almost unchanged (C21: onset temperature = 264°C). Apparently, stabilizer consumption during the first injection-molding step is higher for the homopolymer than for the copolymer. As a result, for the homopolymer, less stabilizer is available for the whole product lifetime.
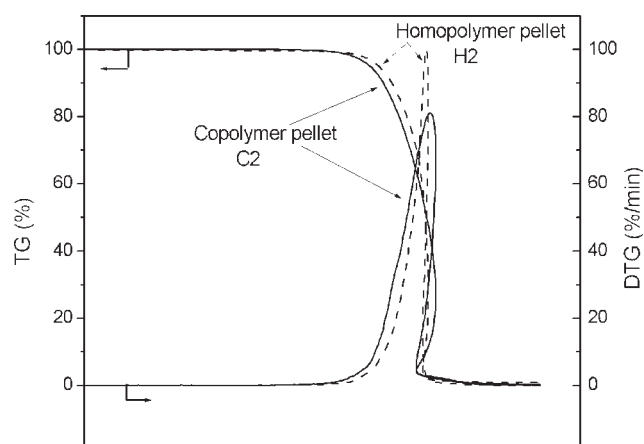

Figure 3 TGA investigations (heating rate = 10 K/min, measurements in air) for the homopolymer and copolymer pellets.
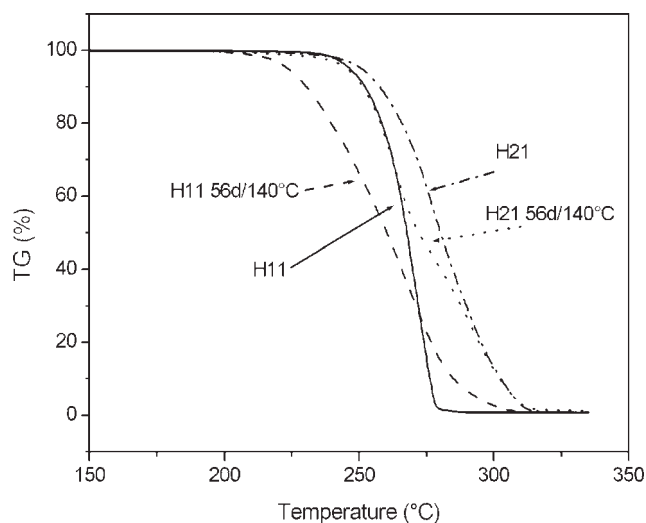
Figure 4 Comparison of the different stabilized homopolymers (H11 and H21) before and after aging by means of TGA (heating rate = 10 K/min, measurements in air).

In Figure 4, the two different stabilized homopolymers are directly compared (in the initial-state and oven-stored conditions). In the initial-state condition, UV-stabilized homopolymer H21 is more thermally stable than heat-stabilized H11, although H21 is also subjected to autoxidation and degradation because of the secondary products of the autoxidation. The different degradation behaviors of the homopolymers are a result of the stabilizers because the TGA measurements reveal that the thermal stabilities of both purified POM homopolymers are comparable.

Kern[9] reported that reagents such as urea, polyamides, and polyurethane prevent splitting by secondary products of the autoxidation. This fact is perhaps the explanation for the higher thermal stability of homopolymer H21. However, these reagents could not be verified with the help of MS.

The influence of thermooxidative aging for the homopolymers and copolymers is illustrated in Figure 5(a,b). For stabilizer consumption, the results of additive-purified pellets are plotted too. The measured TG/derivative thermogravimetry (DTG) signals of the purified pellet represent a borderline case; the removal of the stabilizers allows us to determine their effectiveness by comparison with the initial condition.

As for homopolymer H21 in Figure 5(a), the TG onset temperatures and the DTG plots of the oven-storage condition shift to lower temperatures. After thermooxidative aging, (1) the degradation starts at lower temperatures, and (2) a two-step degradation is noticeable; these two steps can be seen in the TGA results in terms of the different degradation rates.

The DTG peak of the homopolymer without stabilizers (purified pellet) is shifted to lower temperatures. This effect is attributed to the absence of

stabilizers. Therefore, no reorganization processes in the molecule units can take place, and as expected, there is no evidence for reaction products with higher thermal stability [Fig. 5(a)]. A clear dependence on the thermooxidative aging duration can be derived from the shift of the DTG curve toward lower temperatures. In comparison with the purified pellet, even a duration of 21 days in the oven at 140°C leads to stabilizer consumption and a decrease in the onset temperature. A longer storage time (up to 56 days) results in subsequent stabilizer consumption followed by chain damage in the amorphous phase. However, the stabilizer package used in H21 obviously counteracts decomposition of the hydroperoxides and further cleavage of the macromolecule much more strongly than the heat stabilizers in homopolymer H11 (clearly shown in Fig. 4). This experimental result can be explained only in terms of synergetic effects between the heat and UV stabilizers.
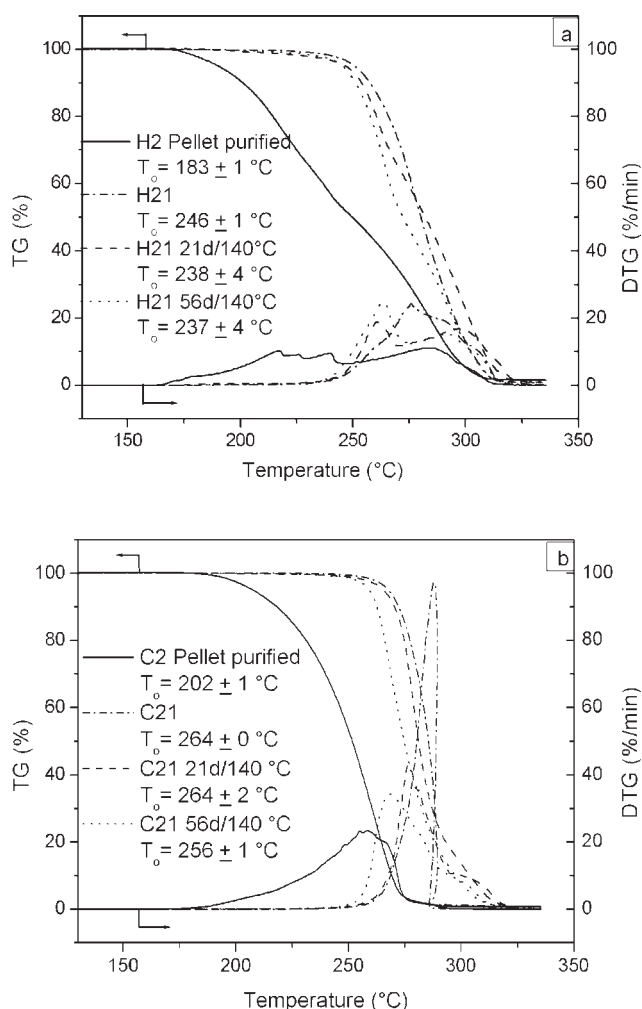

Figure 5 Degradation behavior of POM in the initial state and under various thermooxidative aging conditions (TGA, heating rate = 10 K/min, measurements in air): (a) the homopolymers and (b) the copolymers.
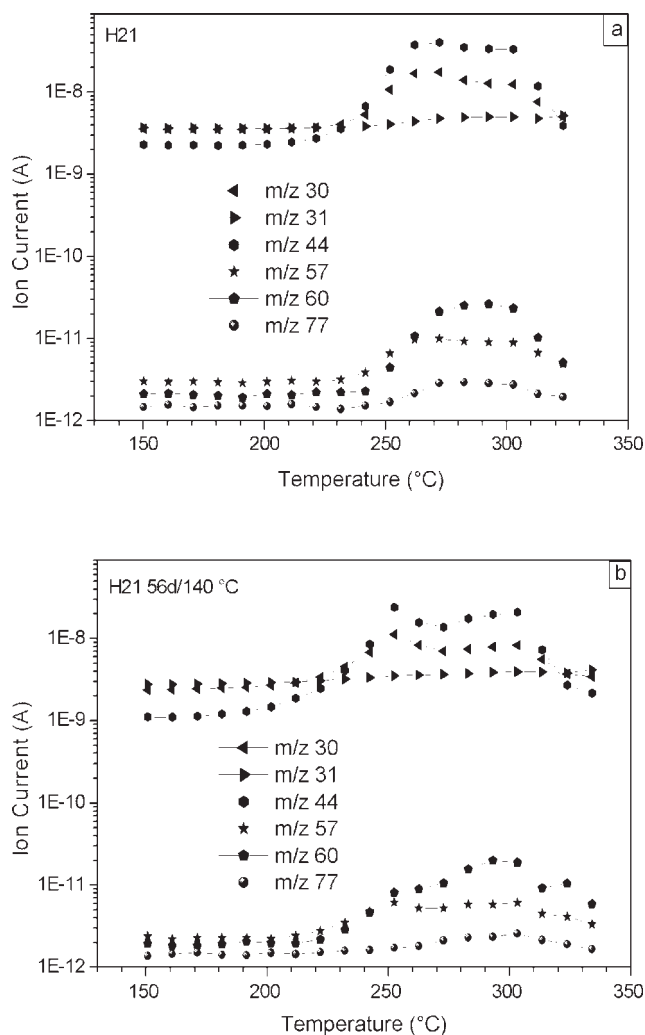
conclude for the copolymers that only some chain scissions take place in the amorphous phase, but further degradation is decelerated.

Regarding the plot for the purified copolymer pellets in which the degradation of the unstabilized macromolecules is illustrated, we can conclude that distinct stabilizer consumption can be observed only for the material aged 56 days.

The corresponding MS traces for the initial condition (H21 and C21) as well as the oven-stored conditions (H21-56d/140°C and C21-56d/140°C) are presented in Figures 6 and 7. Three main fractions can be observed: carbon dioxide ($m/z = 44$), formaldehyde ($m/z = 30$), and trioxane ($m/z = 31$ and $m/z = 60$ as major fragment peaks). TGA/MS measurements performed under an air atmosphere allowed also the observation of water. On a reduced scale, fragments that could be assigned to acetic acid and additive fragments were also detected. A formaldehyde emission can be found as a result of random
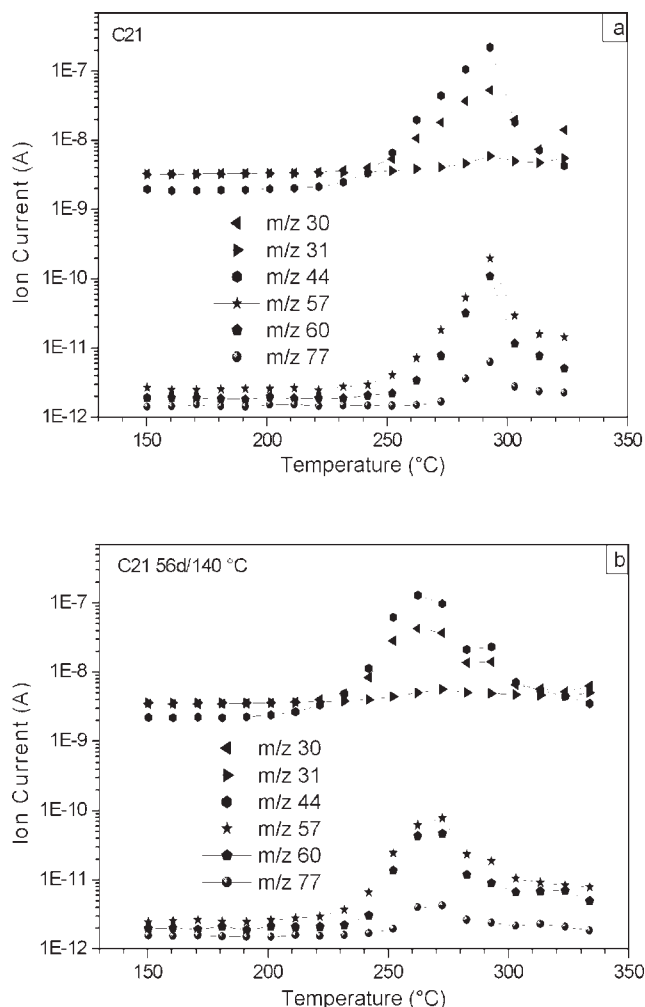
Figure 6 MS spectra of the homopolymer ($m/z = 30$, formaldehyde; $m/z = 31$, major peak trioxane and methoxy fragment; $m/z = 44$, carbon dioxide, ethylene oxide, and urea fragment; $m/z = 57$, additive fragment; $m/z = 60$, acetic acid, methyl formate, and urea; $m/z = 77$, phenyl fragment): (a) initial condition and (b) after oven storage for 56 days at 140°C.

For the copolymer samples (C2), a clear shift of the TG onset temperature toward lower temperatures can be observed only after 56 days of storage at 140°C, although the TG onset temperature of the C21 21d/140°C sample remains nearly constant [Fig. 5(b)]. Because the oven-stored condition (21 days of storage) shows no changes in the DTG plot either, it can be concluded that the UV stabilizer acts as an additional radical scavenger.

Considering that (1) because of the different chain structure, the copolymers are more resistant against thermooxidation, (2) the thermooxidative degradation is initiated by random chain scission in the amorphous phase followed by degradation up to the crystalline surface,[12] and (3) the presence of the stabilizers is favored in the amorphous regions, we can

Figure 7 MS spectra of the copolymer: (a) initial condition and (b) after oven storage for 56 days at 140°C (for the legend, see Fig. 6).
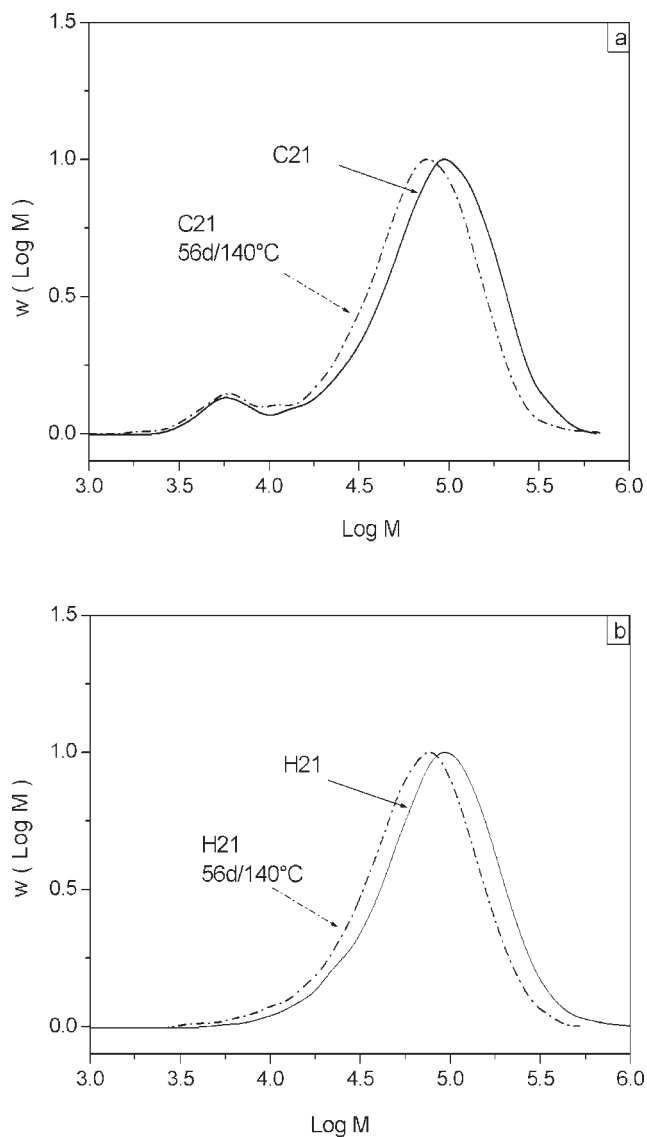
Figure 8 MMD of POM materials in the initial state and after thermooxidative aging: (a) the copolymers and (b) the homopolymers.

scission followed by unzipping. Formaldehyde oxidizes further to formic acid; in the case of the homopolymer, acetic acid ($m/z = 60$) is formed because of the degradation of the existing acetyl end groups. Considering the copolymers, we find that acetic acid will likely be formed because of an oxidation reaction of the C—C—O— units.

In contrast to the heat-stabilized systems reported in ref. 1, in both polymers, additive fragments are detectable ($m/z = 57$ and $m/z = 77$), even after 56 days of storage. The additive fragments ($m/z = 77$ represents a phenyl fragment and $m/z = 57$ represents a t-butyl fragment) are probably issued from the hindered phenol group.

Considering the MS spectra of the homopolymer [Fig. 6(a,b)], we find that the earlier beginning of the decomposition is noticeable by the observation of the displacement of the main MS traces (formaldehyde and carbon dioxide). Furthermore, only negligible consumption of the stabilizer is observed by means of TGA/MS ($m/z = 57$ and $/z = 77$).

The MS traces of the copolymer [Fig. 7(a,b)] also show earlier degradation of the aged sample; the additive fragments ($m/z = 57$ and $m/z = 77$) are still present in comparison with the initial condition. After 56 days at 140°C, the displacement of the MS traces for formaldehyde and carbon dioxide and the altered shape of the DTG signal [Fig. 5(b)] indicate an alteration of some macromolecules. It is concluded that degradation leads to the formation of shorter chains, which decompose at lower temperatures. The synergy effect of existing heat and UV stabilizers leads at the same time to the formation of chains, which are thermally more stable, because the scission of these chains takes place at higher temperatures. The described effects are in accordance with the increased MVR values measured after thermooxidative aging.

The GPC technique was used to determine the molar mass distribution (MMD) of the POM materials. A typical GPC curve shows a bimodal distribution for the copolymer [Fig. 8(a)], as mentioned, for example, in ref. 13; meanwhile, a monomodal distribution is exhibited by the homopolymer, as shown in Figure 8(b). Both polymers exhibit a narrow MMD, with a polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of 2.5 for the copolymer and 1.8 for the homopolymer (Table V). In Figure 8, the MMDs for the aged conditions (H21-56d/140°C and C21-56d/140°C) are also plotted. From the GPC results, it can be confirmed that POM shows thermal aging resistance up to 21 days at 140°C (Table V), but further exposure up to 56 days at 140°C leads to considerable degradation and shifting of the narrow MMD

TABLE V
GPC Investigations of Specimens After 21 and 56 Days of Oven Aging

Material	M_w/M_n	ΔM_w after 21 days at 140°C		M_w/M_n after 21 days at 140°C	ΔM_w after 56 days at 140°C		M_w/M_n after 56 days at 140°C
		g/mol	%		g/mol	%	
H21	1.8	9350	7.0	1.8	27600	24.9	1.9
C21	2.5	7150	5.5	2.5	21900	21.4	2.4

toward a lower molar mass region with a similar distribution curve [Fig. 8(a,b)].

The results are only partially in accordance with the MVR results presented in Table IV. There is a slight change observed for the MVR values determined for POM after 21 days of oven storage at 140°C, but a remarkable shift in the MVR values is displayed after 56 days of thermal aging.

Rätzsch and Eckhardt[14] found that for POM materials, a close correlation exists between the polydispersity and the degradation extent. Materials corresponding to a nonuniformity between 0.5 and 1.0 show no changes in the molar mass until severe degradation proceeds.

Calculations of the nonuniformity from the data available in Table V (the low-molar-mass peak of the copolymer that corresponds to oligomers formed during polymerization has not been considered) result also in values between 0.5 and 1.0 for the examined samples, so according to ref. 14, changes in the MMD can be observed only for extended degradation.

In addition, the low-molar-mass peak of the copolymers remains unchanged after 21 days and even after 56 days of thermal loading.

However, the ion current curves of the MS spectra [Fig. 7(b); aged copolymer] show a second peak after the main degradation peak, which is located close to the temperature (ca. to 290°C) of the decomposition peak of the initial condition [Fig. 7(a)]. This implies that some thermally stable chains still exist or are formed. Because in the MS spectra no changes in the known stable end groups are detectable (e.g., for the homopolymers, an increase in the acetyl and formate groups, and for the copolymers, an increase in the ethyl or acetyl groups), it can be concluded that the formation of cyclic products during aging, particularly in the presence of UV stabilizers, could result from intermolecular transacetalization reactions. Macrocyclic-structure POM, which is partially stable to heat, can be formed by the cationic polymerization of 1,3,5-trioxane in cyclohexane, as reported by Jaacks.[15]

However, although for the homopolymers thermal aging leads to more severe damage, the copolymers are, in relation to thermooxidative attacks under the given aging conditions, substantially more resistant because of their different chain structure.

The degradation behavior of the UV-irradiated homopolymer and copolymer specimens was investigated too. The photooxidation of POM homopolymers and copolymers has been studied by several researchers.[11,16–18] In polyacetaldehyde, it has been found that chain-end-capping acetyl groups are responsible for UV absorption. In POM copolymers containing C—C units, αβ-unsaturated carbon groups are responsible for the initiation of degrada-
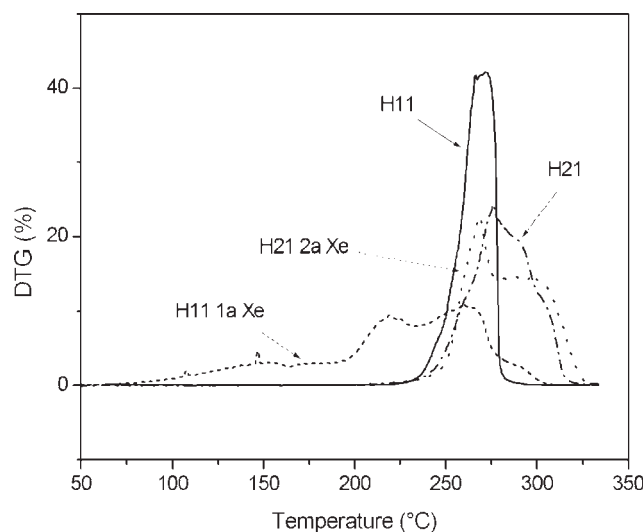

Figure 9 Comparison of the different stabilized homopolymers before and after UV exposure by means of TGA (heating rate = 10 K/min, measurements in air).

tion reactions. Several authors[17,18] are in agreement that chain scission is the predominant reaction. According to Kern and Cherdron,[19] the oxidative degradation of POM occurs through the formation of peroxy and hydroperoxy groups at the activated methyl groups, which then leads to radical-induced chain rupture under the emission of formaldehyde. Moreover, peroxides can oxidize free formaldehyde to formic acid, which catalyzes the acidolytic degradation of the polymer chain. Gardette et al.[17] proposed the following degradation mechanism for photooxidation: the first step leads to the oxidation of the carbon atoms with the formation of secondary hydroperoxides, which decompose into two radicals: an alkoxy macroradical and a hydroxy radical.

The alkoxy macroradical can react in two possible ways: a cage reaction may occur, leading to the formation of carbonate and water, and a β scission may occur, which leads to a formate and an alkoxy macroradical. Hydrogen abstraction from the polymeric chain by macroradicals leads to the formation of alcohols. In this way, a new macroradical is created.

In Figure 9, the results of the TGA investigations are plotted with the DTG signal as a function of the temperature at a heating rate of 10 K/min. With respect to their stabilization conditions, the materials behave differently toward UV weathering (Fig. 9). The dissimilar degradation behaviors of the examined materials, with respect to UV irradiation, result from the differences in the respective stabilizers. The POM specimens that are not specially protected against UV light exhibit surface crazes and chalking after a relatively short weathering period (Fig. 1). Investigations of the chalked layer show that degradation has progressed.[1] UV stabilization significantly
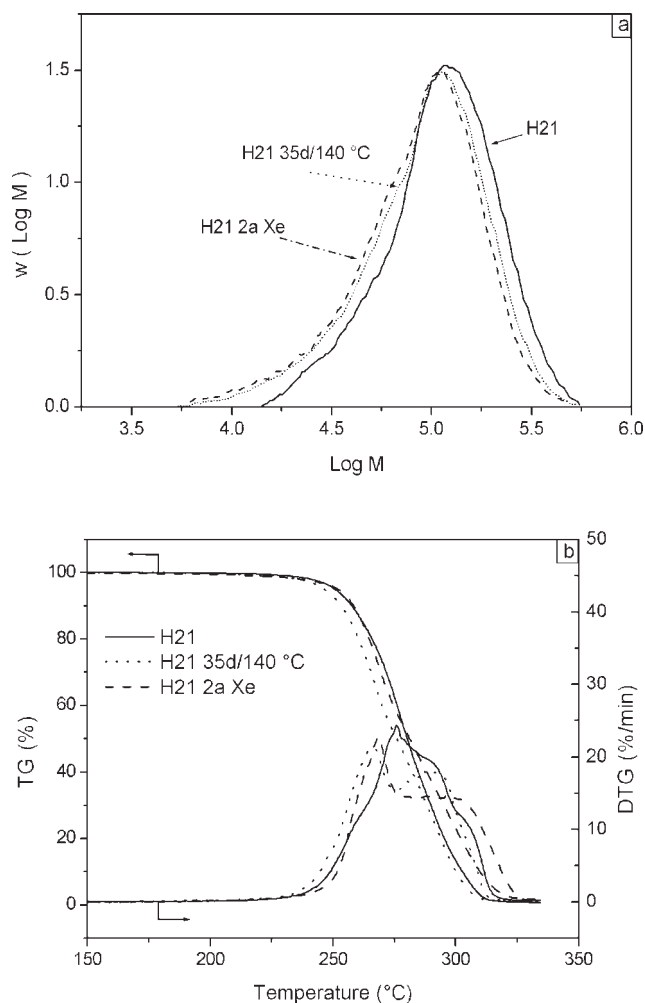
Figure 10 Heat- and UV-stabilized POM homopolymers in the initial state and after thermooxidative aging and UV exposure: (a) GPC and (b) TGA results.

improves the weathering stability. By appropriate UV stabilization, degradation effects leading to the depression of the onset temperature are not found (Fig. 9).

In Figure 10, the MMD [Fig. 10(a)] and TG results [Fig. 10(b)] of the homopolymer are delineated. The same tendency is apparent: thermooxidative aging (35 days at 140°C) and weathering (2a/xenon) cause comparable shifts in the MMD; also, a change in the DTG signal with increasing irradiation exposure and storage duration can be observed. This fact suggests similar damage mechanisms. The damage reactions are due to the presence of carbon atoms in an α position with respect to the oxygen atom, in which hydroperoxidation is quite easy under different oxidation modes, such as thermooxidation and photooxidation. This correlates with the suggestion that photooxidation is also attributable to compounds that form during thermal treatments of the polymer. This is, in fact, common among many polymers that do not have chromophores in the polymer backbone.[3]

CONCLUSIONS

The degradation behaviors of the investigated materials after oven-storage conditions are different and depend on the used stabilizer package. Broad synergy effects between heat and UV stabilizers have been determined. Nevertheless, longer storage duration leads to a strong discoloration of the heat- and UV-stabilized polymers. It is well known that HALS stabilizers and phenolic antioxidants added to polyolefins have a disposition to yellowness under thermal stresses.[20] In this work, it has been shown that this behavior is also verifiable in stabilizer packages for POM. As a result, it is foreseeable that the observed discoloration is proportional to the amount of the stabilizer, which reacts during the aging of the polymer.

In the case of longer thermooxidative aging at elevated temperatures, decomposition of the stabilizers first appears, and it is followed by chain damage and finally the formation of shorter chains with thermally stable end groups. The correlations between the MVR and TGA results support the statement that in the presence of UV stabilizers, the formation of thermally stable chains, such as cyclic products through intermolecular transacetalization reactions, is favored. Such reactions usually take place during the cationic polymerization of cyclic acetals such as 1,3,5-trioxane and 1,3-dioxolane.[13,15]

No correlation between the flattening of the DTG signal after aging and the dispersity of the MMD has been found. After aging, only a shift of the GPC curve toward lower molar masses without a change in the distribution broadness is apparent. Because of the narrow MMD under the initial condition, after thermooxidative aging, a change in the distribution broadness is not probable; thus, no information about the degradation in an early stage can be obtained by means of GPC for the investigated POM materials.

According to the presented results, the following explanation concerning the degradation behavior of the investigated POM homopolymers and copolymers is possible: not only chain scission but also recombination reactions take place because both parts of the macromolecule decompose not entirely, leading to fragments of different chain lengths that can recombine into new polymer chains. The formation of chains with higher thermal stability is also favored because of the existing UV stabilizer.

Through investigations of the degradation behavior of the UV-irradiated homopolymer and copolymer specimens, it has been shown that weathering and thermooxidative aging cause comparable shifts in the MMD and DTG plots. This fact suggests similar damage mechanisms for thermooxidative degradation and photooxidation in POM materials.

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