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Property changes in polyoxymethylene (POM) resulting from processing, ageing and recycling

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Abstract

The degradation processes initiated by thermo-mechanical and thermo-oxidative loading as well as exposure to ultraviolet irradiation weathering were examined in commercially available semi-crystalline polyoxymethylene (POM), using predominantly thermo-analytical methods.

With reference to different injection moulding conditions and moulding geometries (such as loudspeaker grilles and safety-belt components) it is demonstrated that POM-copolymer chain is not affected, even under higher shear stresses and complicated moulding geometries, if an appropriate additive is used.

Thermogravimetric Analysis (TGA) was used to observe stabiliser consumption and further degradation, whereas investigations of melt-flow index and molar mass show effects correlated to late-term changes of the molar mass distribution. Mass-spectrometry investigations performed in parallel to the thermogravimetric analysis identified formaldehyde and carbon dioxide as the main degradation products.

Weathering by ultraviolet irradiation results in damage similar to the thermo-oxidative impact.

Generally, the copolymers are less sensitive to thermo-mechanical and thermo-oxidative degradations than the homopolymers due to the chain modification. Furthermore, reprocessing results in a decrease of the elongation at break and thermo-oxidative induced degradation proceeds faster for the additional UV-stabilised materials.

Keywords: Polyoxymethylene; Reprocessing; Degradation; Thermal ageing; UV-irradiation; Thermal analysis (TGA)

1. Introduction

A specific characteristic of polymeric materials is the alteration of their properties by processing, use and recycling. Because of their polymeric structure, chain damage mechanisms initiated by temperature, shear or UV-light lead to dissociation and in further consequence to failure of the component. The degradation is of thermo-mechanical, thermo-oxidative and photo-oxidative nature.

Kern and Cherdron investigated the degradation behaviour of POM in detail in the early 1960s [1,2]. Copolymers and their specific reduction of the degradation sensitivity were investigated by several authors [3–6]. A good overview about the stabilisers used in POM is given in Refs. [7,8].

It is well known that a large number of reactions take place during processing and small changes in the molecular structure result in considerable modification of properties. In the case of POM, a scheme is presented in Fig. 1 showing the interrelation of reactions.

Many examples can be found in the literature in which a chemical characteristic is used to monitor the degradation progress. In some cases a good correlation with the deterioration of the mechanical properties is found, but knowledge about the correlation between chemical changes and the consequent mechanical changes is very poor. Methods for assessing the changes that are promoted by molecular degradation and under service lifetime are of great importance. The most sensitive methods may indicate that the degradation has occurred long before it is apparent in the engineering properties.

For POM a good approach for the quantification of degradation induced under service lifetime is to determine

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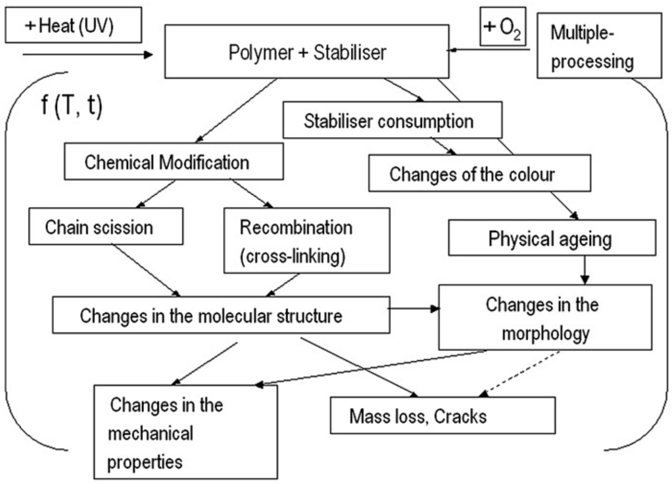

Fig. 1. Scheme of the resulting effects caused by the interactions of thermo-mechanical, thermo-oxidative and photo-oxidative loadings in a polymer.

stabiliser consumption and beginning degradation by means of TGA.

Basically the decrease of the onset temperature in the thermogravimetric Analysis (TGA) is the first indication for thermo-oxidative damage, whereas a decrease of the onset temperature without a change of the first derivative of the TG signal (DTG) refers explicitly to stabiliser consumption. Degradation can be determined by a change of the DTG signal [9].

2. Experimental

2.1. Materials

Two differently stabilised homopolymers DELRIN® 900P (solely heat stabiliser) and DELRIN® 927 P and 127 P (heat & UV-stabiliser) and four copolymer types Ultraform® W2320 003 (solely heat stabiliser), Ultraform® W2320 U03 (heat & UV-stabiliser) and Hostaform® 27021(solely heat stabiliser) and Hostaform® 27021 LS (heat & UV-stabiliser) were used for the investigations. The resins are commercially available and designated for injection moulding. The samples for the experiments were injection moulded specimens (sample geometry according to ISO 527-2, Type 1A), injection moulded loudspeaker grilles and injection moulded safety-belt components (press button). All samples were produced in accordance with processing conditions recommended by the producer (homopolymers: temperature of the nozzle 190 °C, mould temperature 90 °C; copolymers: temperature of the nozzle 215 °C, mould temperature 90 °C). In order to exclude hydrolytic degradation all materials were pre-dried for 4 h at 80 °C before moulding. An overview of the sample geometries and assignments is given in Table 1. All investigated materials had similar Melt Volume Rates (20–25 cm^3/10 min) except the heat & UV-stabilised DELRIN® 127 P with a MVR of 5 cm^3/10 min and are available for comparable applications.

Table 1
Materials of interest

	Material	Stabiliser	Acronym	Investigated geometries
A	Copolymer	Heat	A1 pellet	Pellet
			A11 first processing step	Specimens
			A17 seventh processing step	
	Copolymer	Heat + UV	A2 pellet	Pellet
			A21 first processing step	Specimens
			A27 seventh processing step	
B	Copolymer	Heat	B1 pellet	Pellet
			B11 first processing step	Specimens
			B17 seventh processing step	Loudspeaker grilles
	Copolymer	Heat + UV	B2 pellet	Pellet, specimens
			B21 first processing step	Loudspeaker grilles
			B27 seventh processing step	Press button
H	Homopolymer	Heat	H1 Pellet	Pellet
			H11 first processing step	Specimens
			H17 seventh processing step	
	Homopolymer	Heat + UV	H2 pellet	Pellet
			H21 first processing step	Specimens
			H27 seventh processing step	Press button

Thermal ageing was performed at 140 °C (maximum temperature deviation: 1.5 °C) in an oven (Heraeus) for 21, 35 and 56 d. Samples will be labelled as 21 d/140 °C, 35 d/140 °C and 56 d/140 °C in the following.

For UV-irradiation an artificial weathering test using a Xenontester (Suntest XLS+, Atlas) was carried out. This test simulates the standard climatic conditions of car indoor irradiation for Central Europe (irradiation dose equivalent for 1 year 1709 MJ/m^2, black panel temperature ~50 °C). Samples exposed to UV-irradiations will be denoted as 1a UV (=1 year) and 2a UV (=2 years).

2.2. Methods

Non-isothermal TGA: Samples of about 10 mg were heated in air and nitrogen atmosphere with a purge gas stream of 100 ml/min in ceramic pans with a heating rate of 10 K/min. The thermogravimetric measurements were performed using a TGA 2050 (TA-Instruments). The onset temperature (i.e. the degradation start temperature) was defined as the temperature at which a mass loss of 3% of the initial sample mass was reached [10]. Coupling with a mass-spectrometer (MS) provided a simultaneous analysis of specific degradation products that evolved during thermal degradation. The mass spectrum reflects the mass-to-charge ratio and the relative abundance of the ion fragments, thus providing a fingerprint of each compound. Gases evolving during the decomposition of the sample were registered after every 10 °C step of temperature increase. The MS used was a Thermostar (Balzers). The coupling consisted of a heated quartz capillary tube (120 °C) connecting the TGA furnace outlet with the MS gas inlet through a pinhole diaphragm.