

Headspace Solid-Phase Microextraction with Gas Chromatography/Mass Spectrometry Reveals a Correlation between the Degradation Product Pattern and Changes in the Mechanical Properties during the Thermooxidation of In-Plant Recycled Polyamide 6,6

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ABSTRACT: The increased susceptibility of in-plant recycled polyamide 6,6 toward thermooxidation was shown by headspace solid-phase microextraction with gas chromatography/mass spectrometry (HS-SPME/GC-MS), tensile testing, differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR). A correlation between the deterioration in mechanical properties and the formation of degradation products due to thermooxidation was found, and the most prominent decrease in mechanical properties coincided with the largest increase in the abundance of degradation products. The recycled materials had a shorter induction period toward oxidation, and their mechanical properties deteriorated faster than the mechanical properties of virgin material. The same trend was observed with HS-SPME/GC-MS because degradation products were found for recycled materials after oxidation times shorter than those for virgin material. Furthermore, larger amounts of degradation products were formed in the recycled materials. The high sensitivity of HS-SPME/GC-MS as an analytical tool was demonstrated because it was able to detect changes caused by oxidation considerably earlier than the

other methods. Unlike DSC and FTIR, it could also show differences between samples recycled for different times. Four groups of degradation products—cyclic imides, pyridines, chain fragments, and cyclopentanones—were identified in thermooxidized polyamide 6,6. After 1200 h of thermooxidation, 1-pentyl-2,5-pyrrolidinedione was the most abundant degradation product. Approximately four times more 1-pentyl-2,5-pyrrolidinedione was formed in polyamide recycled three times than in virgin polyamide. Pyridines and chain fragments behaved toward oxidation and repeated processing like cyclic imides; that is, their amounts increased during oxidation, and larger amounts were formed in recycled materials than in virgin material. The cyclopentanone derivatives were present already in unaged material, and their amounts decreased during oxidation. Cyclopentanones were not formed because of the thermooxidation of polyamide 6,6. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3396–3407, 2002

Key words: chromatography; degradation; nylon; polyamides; recycling

INTRODUCTION

The use of plastic materials has increased rapidly over the last few decades. With the high usage of plastics come also requirements for the recycling of plastics to avoid filling landfills with slowly degrading plastic waste. Most studies on recycling have been performed on large-volume plastics, and today polyethylene and polypropylene are recycled to a large extent. It is rather well known how these materials behave during recycling and how their mechanical properties are affected by repeated processing. During the last decade, the demands for recycling have increased further, and now attention has turned to the more expensive engineering plastics such as polyamide. Eriksson

et al.¹ showed that recycling has a dramatic influence on the mechanical and thermal properties of unstabilized polyamide 6,6. However, glass-fiber-reinforced polyamide 6,6 may be recycled up to four times without any significant deterioration in the performance of the material.² Proper amounts and combinations of processing additives and antioxidants, together with optimized processing parameters, make it possible to recycle polyamides without significant losses of mechanical properties.

To obtain a thorough understanding of the degradation process, we need to correlate the chemical, mechanical, and physical changes taking place in the polymer matrix with the formation of low-molecular-mass degradation products. The changes taking place in the polyamide matrix due to photooxidation and thermooxidation have been the subject of several studies.^{3–10} The low-molecular-mass products formed by the pure thermal degradation of polyamide 6,6, that is, in the absence of oxygen, are also rather well estab-

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lished,^{11–17} but considerably less attention has been given to identifying the thermooxidation products of polyamide. However, in a recent study, we identified several low-molecular-mass products formed during the long-term thermooxidation of polyamide 6,6.¹⁸ The identified thermooxidation products indicated that the thermooxidative degradation of polyamide 6,6 starts at the N-vicinal methylene group in the polyamide backbone. Furthermore, it was concluded that long-term oxidation proceeds from the N-vicinal methylene into the hexamethylenediamine part of the polyamide backbone, giving specific groups of degradation products with structures that can be deduced from the original polymer structure. Another recent study showed that the photooxidation of polyamide 6,6 also starts at the N-vicinal methylene group.¹⁹

The aim of this study was to determine if the degradation product pattern of recycled polyamide 6,6 can be correlated to the simultaneous changes in mechanical properties during thermooxidation. This could provide new means of testing the quality of recycled materials. Headspace solid-phase microextraction with gas chromatography/mass spectrometry (HS-SPME/GC-MS) was applied to identify the degradation products and to trace changes in recycled materials at early stages of thermooxidation. The influence of recycling on the degradation process, degradation product pattern, and susceptibility toward thermooxidation was studied.

EXPERIMENTAL

Materials

Granules of a commercially available unstabilized polyamide 6,6 (Zytel 101L) were generously supplied by DuPont (Stockholm, Sweden). The material was not stabilized against thermal oxidation, but it did contain a lubricant, probably an aliphatic oil, which was added to the material to facilitate processing operations.

Extrusion of samples

Four series of samples were prepared by repeated extrusion of the polyamide 6,6 granules. The samples were extruded one, two, three, or four times and were denoted V, R1, R2, and R3, respectively. The extrusions were performed with a DSK 35/9 D counterrotating twin-screw extruder from Brabender (Duisburg, Germany). The extruder was equipped with an adjustable flat-sheet die head (100 mm × 0.2 mm), giving 200- μ m-thick sheets. During the extrusion, the three heated zones of the screw were all set to 285°C. The screw speed was 30 mm/min. After each extrusion, some of the polyamide sheet was removed from the material stream for aging, whereas the rest of the

material was milled in a Moretto (Padova, Italy) granulator mill and reextruded. Before each extrusion, the granules were dried for 8 h at 90°C in a Piovan (Venezia, Italy) granulate dryer.

Thermooxidation

Samples for the extraction of degradation products were cut from the extruded polyamide sheets as strips approximately 1.5 cm × 5 cm in size. The strips (2 ± 0.1 g) were placed in 20-mL headspace glass vials from Chrompack (Middleburg, The Netherlands) and closed with a polytetrafluoroethylene (PTFE)–silicone rubber septum cap from Perkin Elmer (Wellesley, MA). Samples for tensile testing, differential scanning calorimetry (DSC) measurements, and Fourier transform infrared (FTIR) measurements were made by dog-bone-shaped specimens being punched from the sheets. The dog-bone-shaped specimens were 5 mm wide and had a gauge length of 25 mm. The samples were placed in a conventional circulating air oven from Heraeus (Hanau, Germany) with a minimum of 1 cm between adjacent samples. The headspace vials were placed in the same oven and oxidized at $100 \pm 2^\circ\text{C}$ for 25, 100, 500, and 1200 h. Tensile testing, DSC, and FTIR measurements were performed also after 5 h of aging.

Extraction

Poly(dimethylsiloxane divinylbenzene) SPME fibers from Supelco (Bellafonte, PA) were used to extract low-molecular-mass products from polyamide 6,6. The degradation products were extracted by the subsection of the fiber to the headspace over the polyamide strips for 30 min at 80°C. To measure changes in the abundance of degradation products from the polyamide during oxidation, we added an internal standard to each sample before extraction. With an internal standard, possible errors in the extraction could be eliminated. The relative peak areas of the peaks were calculated by the area of the internal standard being divided by the areas of the peaks. The internal standard also served as an indicator of the repeatability in the performance of the SPME fiber. The internal standard used was an ester, methyl-heptanoate, from Polyscience Corp. (Niles, IL). An internal standard solution was prepared by the dilution of 5 μL of the ester with 10 mL of chromatography-grade LiChrosolv water from Merck (Darmstadt, Germany). The standard solution (1 μL) was added to each vial before extraction.

GC-MS

The GC-MS analyses were performed on a GCQ instrument from ThermoFinnigan (San José, CA). The

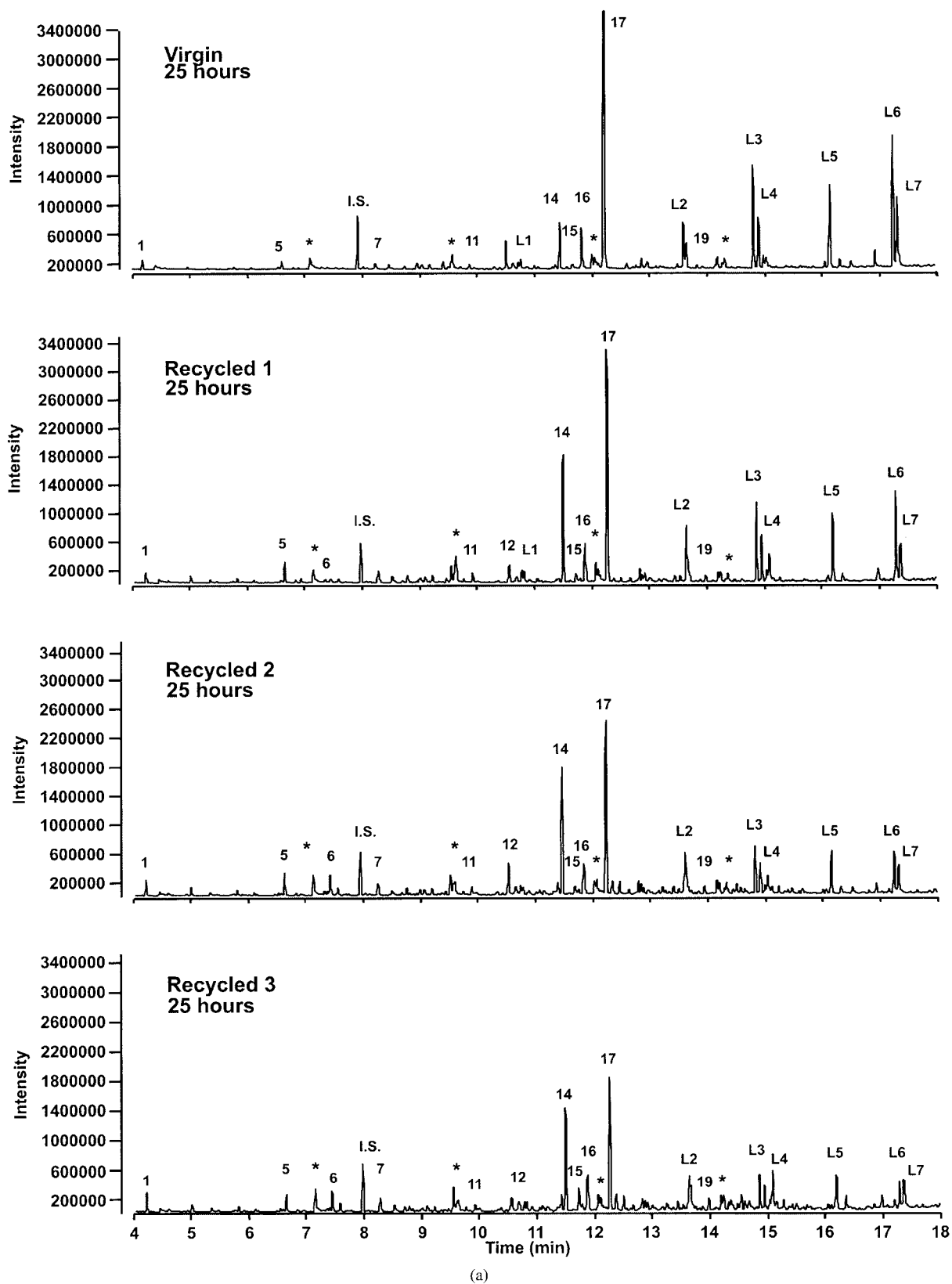


Figure 1 Total ion chromatograms of extracted low-molecular-weight compounds from virgin and recycled polyamide 6,6 after (a) 25 and (b) 1200 h of thermal oxidation at 100°C.

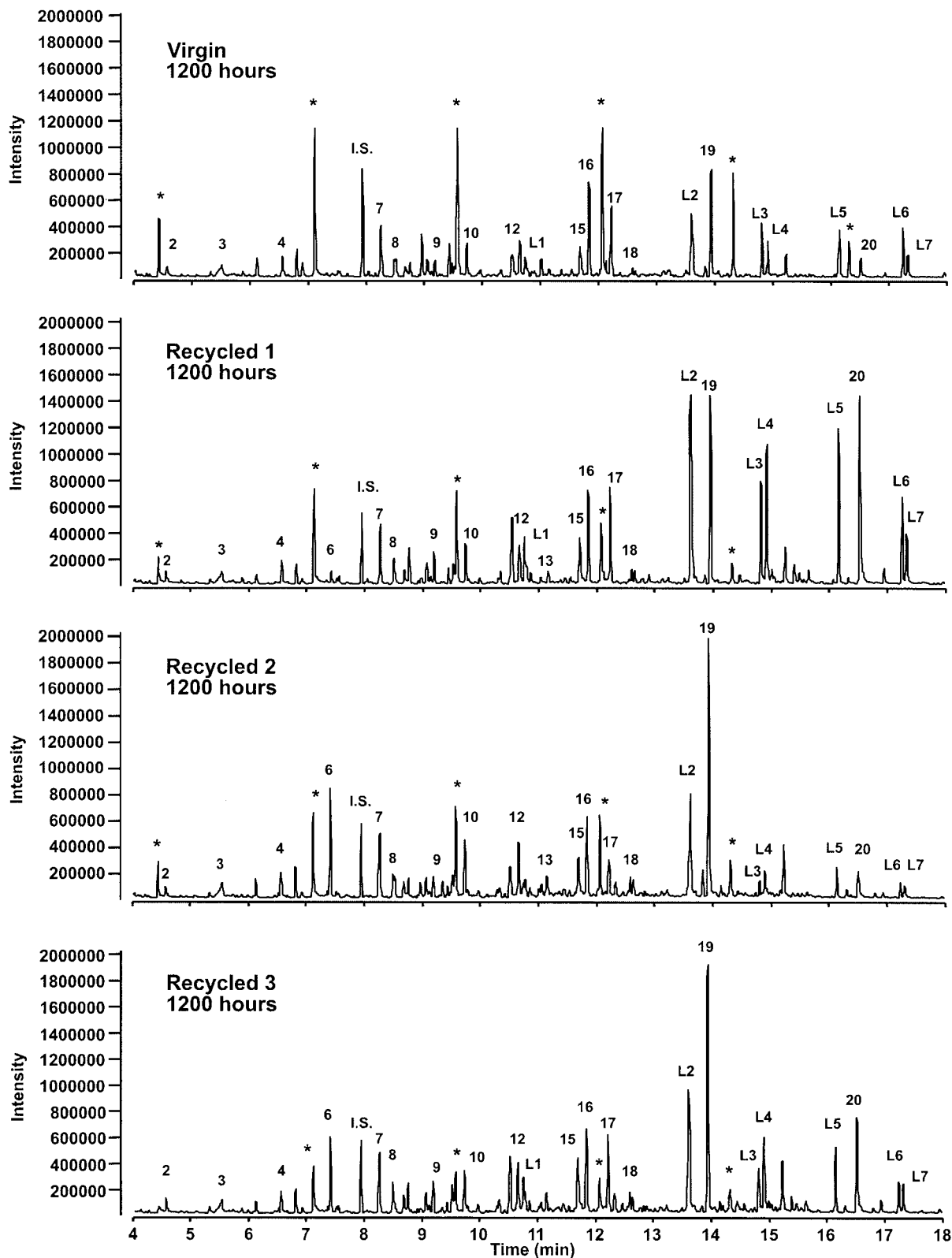


Figure 1 (Continued from the previous page)

column used was a wall-coated, open-tubular, fused-silica, low-bleed Cp-Sil 8CB/MS column (30 m × 0.25-mm inner diameter, 0.25-μm film thickness)

from Chrompack. The column temperature was initially held at 40°C for 3 min. The temperature was then increased to 250°C at a heating rate of 10°C/min and

was held at 250°C for 10 min. Helium (99.9999%) was used as a carrier gas with a constant velocity of 40 cm/s. The extracted degradation products were desorbed from the SPME fiber by the fiber being placed in the injector of the gas chromatograph for 5 min at 220°C. The injector was operated in the splitless mode. To identify and quantify the products, we ran the mass spectrometer in the electronic ionization (EI) mode at an electron energy of 70 eV. The detector scanned from 35 to 400 m/z with a scan cycle of 0.43 s. Some samples were also run in the chemical ionization (CI) mode with methane as a reagent gas to confirm the molecular ions.

Identification of degradation products

The identity of most of the products was confirmed by a comparison of the recorded mass spectrum and retention time of the degradation product with the mass spectrum and retention time of a standard compound run under the same conditions. The same GC-MS method was used for the standard compounds and degradation products. The identification was positive, as the mass spectrum and retention time of the authentic compound were identical to those of the unknown degradation product. Not all of the degradation products could be identified by comparison to authentic compounds because they were not commercially available. These products were identified by the comparison of their mass spectra to the mass spectra included in a reference library, NIST 98, developed at the National Institute of Standards and Technology (Gaithersburg, MD). The identity of some of the compounds could be further confirmed by literature mass spectra.

Tensile testing

The tensile properties were measured on an Instron series IX tensile testing instrument (Bristol, United Kingdom). The oven-aged samples were drawn to break at a crosshead speed of 10 mm/min. All samples were measured dry as molded and tested at 50% relative humidity and 23°C.

DSC

A Mettler Toledo (Columbus, OH) DSC instrument with an 820 module was used to measure the melting peak temperatures of the samples. Circular disks with a diameter of 4 mm were punched out from the films, and this gave samples of approximately 5–6 mg. The size of the disks was chosen to fit the measuring pans. All measurements were performed under a nitrogen atmosphere at a nitrogen flow rate of 50 mL/min through the measuring cell. The instrument was programmed to condition the sample at 25°C for 5 min

and then raise the temperature to 300°C at a heating rate of 10°C/min. The sample was held at 300°C for 3 min and then cooled to 25°C at 10°C/min. The cycle of heating and cooling was then repeated. The melt peak temperatures from the second heating cycle were used to eliminate the thermal history of the samples.

FTIR spectroscopy

During oxidation, different carbonyl groups were formed in the polymer chain. These included acid groups at 1705 cm^{-1} , ketones at 1718 cm^{-1} , and aldehydes at 1728 cm^{-1} . The formation of these groups was measured with a PerkinElmer FTIR spectrometer with a 4 \times beam condenser. The instrument was equipped with a micro-attenuated total reflection (ATR) holder and a KRS-5 prism with an incident angle of 45°. The carbonyl index was calculated as the ratio of the height of the carbonyl peak at 1718 cm^{-1} to the height of the amide peak at 1200 cm^{-1} .

RESULTS AND DISCUSSION

Low-molecular-mass degradation products in polyamide 6,6

Figure 1 shows the GC-MS chromatograms of the low-molecular-mass products extracted from virgin and recycled polyamide 6,6 after 25 and 1200 h of thermooxidation at 100°C. A comparison of Figure 1(a,b) clearly shows how the number and quantity of products increased as a function of thermooxidation and repeated extrusion. Low-molecular-mass products were also extracted from virgin and recycled materials before oxidation to determine if some of the products were already present in the unaged materials. These products were formed during the processing or polymerization of the material. In these chromatograms, only a few peaks with small peak areas are present. After 25 h of oxidation, 9 degradation products in low amounts were detected in the virgin polyamide 6,6, and 12 degradation products were detected in the polyamide 6,6 recycled three times. After 1200 h of oxidation, 14 degradation products in the virgin polyamide 6,6 and 16 degradation products in the polyamide 6,6 recycled three times were identified. The amounts of most of the products increased during the oxidation. Several peaks, identified as linear alkanes and alkenes with lengths ranging from 10 to 17 carbons, also appeared in the chromatograms. These compounds were denominated L1–L7 in the chromatograms, and they originated from lubricants added to the polymer. Altogether, 20 different polyamide degradation products were identified. The names and relative areas of the identified products are given in Table I.

TABLE I
Identified Degradation Products from the Thermal Oxidation of Virgin and Recycled Polyamide 6,6 at 100°C and Their Relative Areas

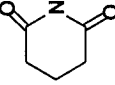
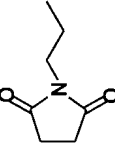
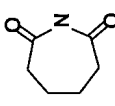
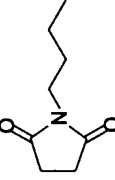
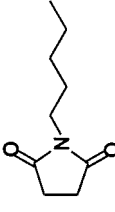

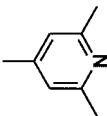
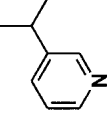
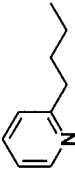
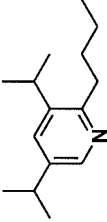

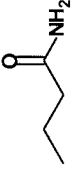


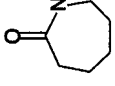
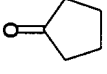
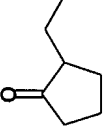
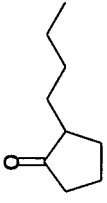
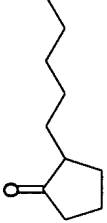
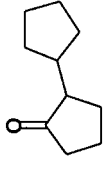
No.	Compound	Virgin material						Recycled 1						Recycled 2						Recycled 3					
		Retention time t_R (min)						Oxidation time (h)						Oxidation time (h)						Oxidation time (h)					
		25	100	500	1200	25	100	500	1200	25	100	500	1200	25	100	500	1200	25	100	500	1200				
1	Cyclopentanone ^a	19 ± 2	11 ± 1	0	0	33 ± 7	11 ± 1	4 ± 1	0	42 ± 2	16 ± 1	5 ± 1	0	57 ± 9	29 ± 1	0	0								
4.2																									
2	2-Methyl-pyridine ^b	0	9 ± 1	9 ± 1	15 ± 1	0	0	17 ± 3	24 ± 5	0	0	18 ± 2	24 ± 2	0	19 ± 2	22 ± 3	27 ± 5								
4.6																									
3	Pentanoic acid ^a	0	0	0	29 ± 5	0	9 ± 1	28 ± 6	54 ± 5	0	10 ± 1	34 ± 9	62 ± 7	0	0	27 ± 2	63 ± 10								
5.5																									
4	Butanamide ^a	0	0	15 ± 2	23 ± 2	0	0	20 ± 2	41 ± 2	0	0	18 ± 2	42 ± 5	0	0	18 ± 0	44 ± 6								
6.6																									
5	2-Ethyl-cyclopentanone ^b	17 ± 3	13 ± 1	0	0	58 ± 8	34 ± 1	10 ± 1	0	54 ± 3	35 ± 3	10 ± 1	0	48 ± 7	47 ± 3	11 ± 1	0								
6.6																									
6	2,4,6-Trimethyl-pyridine ^a	0	0	0	0	16 ± 3	17 ± 2	27 ± 2	18 ± 3	57 ± 4	99 ± 6	212 ± 19	130 ± 32	56 ± 9	129 ± 14	116 ± 6	91 ± 17								
7.4																									
7	Pentanamide ^a	12 ± 3	37 ± 5	49 ± 6	66 ± 2	0	45 ± 3	88 ± 10	115 ± 8	38 ± 2	48 ± 3	83 ± 6	126 ± 13	43 ± 4	76 ± 3	82 ± 5	126 ± 8								
8.3																									
8	3-(1-Methylethyl)pyridine ^b	0	0	0	37 ± 2	0	0	31 ± 5	65 ± 3	0	0	37 ± 3	69 ± 6	0	40 ± 3	41 ± 3	73 ± 5								
8.5																									
9	2-Butyl-pyridine ^b	0	0	0	16 ± 1	0	0	29 ± 4	36 ± 11	0	0	26 ± 2	31 ± 4	0	25 ± 3	27 ± 3	39 ± 10								
9.2																									
10	N,N-Hexamethylenebisformamide ^b	0	17 ± 1	23 ± 3	38 ± 4	0	0	131 ± 51	90 ± 16	0	0	43 ± 5	93 ± 8	0	0	34 ± 6	91 ± 16								
9.7																									
11	2-Butyl-cyclopentanone ^b	10 ± 1	8 ± 1	0	0	26 ± 2	17 ± 1	0	0	21 ± 1	14 ± 1	0	0	19 ± 2	20 ± 2	0	0								
9.9																									
12	Glutarimide ^a	0	0	35 ± 8	46 ± 7	31 ± 0	29 ± 2	56 ± 7	80 ± 6	40 ± 4	32 ± 3	58 ± 3	103 ± 9	38 ± 3	58 ± 2	116 ± 10									
10.6																									
13	1-Propyl-2,5-pyrrolidinedione ^b	0	0	0	0	0	0	11 ± 1	29 ± 8	0	0	28 ± 3	38 ± 4	0	26 ± 1	25 ± 1									
11.2																									
14	2-Pentyl-cyclopentanone ^a	89 ± 6	8 ± 1	9 ± 2	0	324 ± 40	199 ± 15	52 ± 12	0	290 ± 18	182 ± 14	51 ± 6	0	270 ± 34	252 ± 21	58 ± 8	0								
11.5																									
15	Caprolactam ^a	17 ± 3	33 ± 3	26 ± 5	38 ± 3	27 ± 4	26 ± 2	49 ± 15	79 ± 19	27 ± 5	34 ± 3	51 ± 8	93 ± 11	54 ± 9	105 ± 6	91 ± 9	127 ± 13								
11.7																									
16	Azepane-2,7-dione ^b	96 ± 7	149 ± 6	107 ± 18	100 ± 7	100 ± 12	90 ± 3	126 ± 31	122 ± 38	89 ± 3	85 ± 6	111 ± 4	124 ± 12	104 ± 13	159 ± 0	124 ± 8	137 ± 14								
11.8																									
17	2-Cyclopentyl-cyclopentanone ^a	1323 ± 82	1053 ± 38	306 ± 46	82 ± 7	647 ± 83	458 ± 13	244 ± 60	96 ± 49	458 ± 31	358 ± 24	174 ± 15	71 ± 4	374 ± 44	438 ± 37	198 ± 32	95 ± 29								
12.2																									
18	1-Butyl-2,5-pyrrolidinedione ^{b,c}	0	0	4 ± 1	11 ± 1	0	0	20 ± 15	24 ± 1	0	0	15 ± 0	31 ± 2	0	12 ± 1	15 ± 3	34 ± 5								
12.6																									
19	1-Pentyl-2,5-pyrrolidinedione ^c	4 ± 2	29 ± 2	63 ± 11	106 ± 8	18 ± 2	34 ± 3	162 ± 25	338 ± 18	19 ± 2	45 ± 6	179 ± 7	402 ± 26	30 ± 2	116 ± 12	154 ± 40	453 ± 58								
14.0																									
20	2-Butyl-3,5-dimethyl-ethylpyridine ^b	0	0	85 ± 15	45 ± 10	0	0	148 ± 60	142 ± 20	0	0	104 ± 38	48 ± 14	72 ± 5	0	89 ± 26	80 ± 13								
16.5																									

^a Identified by comparison to the authentic compound.

^b Identified by comparison to the NIST database.

^c Identified by comparison to spectra found in the literature.

TABLE II
Identified Degradation Products from Polyamide 6,6

Cyclic imides					
2,6-Piperidinedione		1-Propyl-2,5-pyrrolidinedione	Azepane-2,7-dione	1-Butyl-2,5-pyrrolidinedione	1-Pentyl-2,5-pyrrolidinedione
Pyridines					
2-Methylpyridine		2,4,6-Trimethylpyridine	3-(1-Methylethyl)pyridine	2-Butylpyridine	2-Butyl-3,5-dimethylethylpyridine
Chain fragments					
Pentanoic acid		Butanamide	Pentanamide	<i>N,N</i> -Hexamethylenebisformamide	Caprolactam
Cyclopentanone and some of its derivatives					
Cyclopentanone		2-Ethylcyclopentanone	2-Butylcyclopentanone	2-Pentylcyclopentanone	2-Cyclopentylcyclopentanone

The products are divided into four different groups, where products sharing a common structural feature belong to the same group.

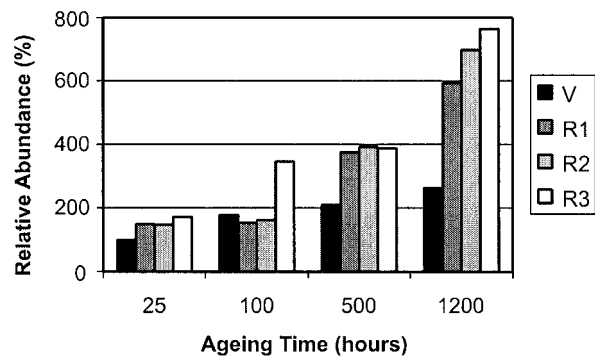


Figure 2 Relative amounts of cyclic imides extracted from virgin and recycled polyamide 6,6 after 25, 100, 500, and 1200 h of thermooxidation at 100°C.

Influence of recycling on the formation of degradation products

The identified degradation products were categorized into four groups (cyclic imides, pyridine derivatives, chain fragments, and cyclopentanone derivatives) according to Table II. Five cyclic imides [2,6-piperidinedione (glutarimide), azepane-2,7-dione, 1-propyl-2,5-pyrrolidinedione, 1-butyl-2,5-pyrrolidinedione, and 1-pentyl-2,5-pyrrolidinedione] were detected after oxidation. Figure 2 shows the total amounts of cyclic imides extracted after the thermooxidation of virgin and recycled polyamide 6,6. The amounts of cyclic imides clearly increased as a function of the thermooxidation time, and larger amounts of cyclic imides were formed during the thermooxidation of recycled polyamide than during the thermooxidation of virgin polyamide 6,6. In particular, 1-pentyl-2,5-pyrrolidinedione showed a large increase in abundance. At the beginning of the oxidation, it was found only at trace levels, but after 1200 h, its relative peak area had increased drastically, making it the most abundant degradation product. The increase was prominent for both virgin and recycled materials, but, as shown in Figure 3, substantially more 1-pentyl-2,5-pyrrolidinedione was formed from the recycled materials than from the virgin material. The amount of 1-pentyl-

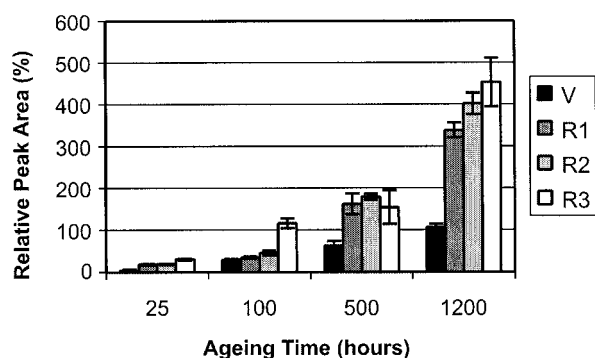


Figure 3 Relative peak area of 1-pentyl-2,5-pyrrolidinedione extracted from virgin and recycled polyamide 6,6 after 25, 100, 500, and 1200 h of thermooxidation at 100°C.

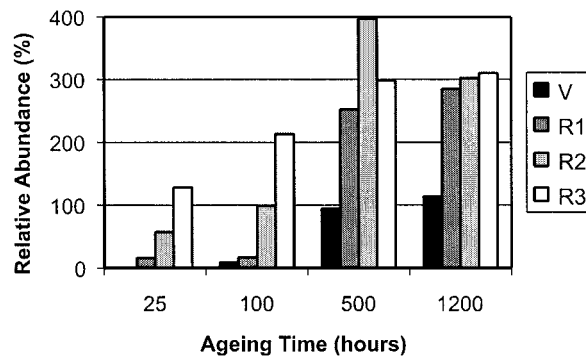


Figure 4 Relative amounts of pyridines extracted from virgin and recycled polyamide 6,6 after 25, 100, 500, and 1200 h of thermooxidation at 100°C.

2,5-pyrrolidinedione that formed during the oxidation corresponded almost linearly to the number of recycling steps of the respective samples. Lower amounts of glutarimide, 1-propyl-2,5-pyrrolidinedione, and 1-butyl-2,5-pyrrolidinedione were detected, and they showed similar behavior toward oxidation and recycling as 1-pentyl-2,5-pyrrolidinedione; that is, their amount increased during thermooxidation and repeated processing. Approximately the same amount of azepane-2,7-dione was detected in virgin and recycled materials, and the amount remained almost constant throughout the oxidation. This suggests that azepane-2,7-dione is formed through a different mechanism than the other succinimides within this group. It can be formed by ring closure of the adipamide produced as the polyamide 6,6 backbone is cleaved by oxidation of the N-vicinal methylene group of two neighboring hexamethylenediamine units or as a result of oxidation of caprolactam.²⁰

As shown in Figure 4, the amount of pyridines increased as a function of the oxidation time, and larger amounts of pyridines were found in recycled materials than in virgin material. However, the repeated recycling did not significantly increase the formation of pyridines, as the amounts of pyridines were approximately equal in all the recycled materials. Most of the pyridine derivatives were not detected before 100 or 500 h of aging. However, 2,4,6-trimethylpyridine was extracted from all recycled materials after only 25 h. It was not detected in the virgin material even after the longest oxidation time of 1200 h. 2-Butyl-3,5-dimethylethylpyridine was generally not found before 500 h of aging, but then at rather large amounts in all samples. The amount of 2-butyl-3,5-dimethylethylpyridine decreased with prolonged aging, probably because of further degradation to 3-(1-methylethyl)-pyridine and 2-butylpyridine.

The chain fragments all had structural features that could be deduced from the repeating unit of the polyamide chain. They also have a carbonyl group at their endpoints and were, therefore, most likely formed as a result of chain cleavage in the vicinity of the amide

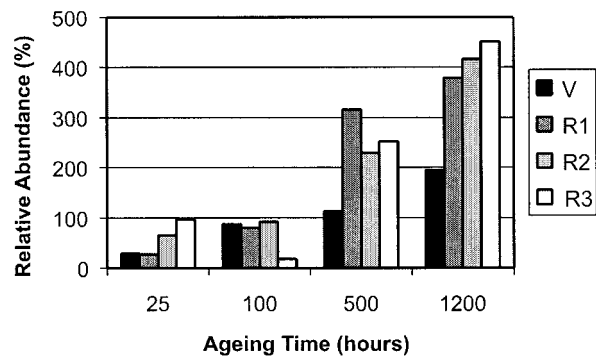


Figure 5 Relative amounts of chain fragments extracted from virgin and recycled polyamide 6,6 after 25, 100, 500, and 1200 h of thermooxidation at 100°C.

group; that is, the degradation took place mainly at the N-vicinal methyl group. They all showed similar behavior during oxidation, and the amounts of all the chain fragments increased with the oxidation time, as shown in Figure 5. More chain fragments were formed in recycled polyamide 6,6 than in virgin polyamide 6,6, but there was no significant difference between materials that were recycled once, twice, or three times. After 1200 h, pentanamide and caprolactam were the most abundant chain fragments in all samples.

Cyclopentanone and four substituted cyclopentanones were identified in the unaged material: 2-ethyl-cyclopentanone, 2-butyl-cyclopentanone, 2-pentyl-cyclopentanone, and 2-cyclopentyl-cyclopentanone. Contrary to the other products, the amounts of all the cyclopentanones decreased during thermooxidation, as shown in Figure 6. This means that cyclopentanones were formed already during polymerization or processing, and they were not formed during the thermooxidation of polyamide 6,6 at 100°C. As seen in Figures 7 and 8, the amounts of most of the cyclopentanones, that is, cyclopentanone, 2-ethyl-cyclopentanone, 2-butyl-cyclopentanone, and 2-pentyl-cyclo-

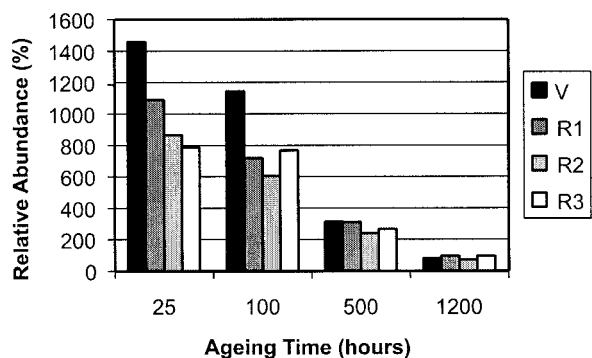


Figure 6 Relative amounts of cyclopentanone and cyclopentanone derivatives extracted from virgin and recycled polyamide 6,6 after 25, 100, 500, and 1200 h of thermooxidation at 100°C.

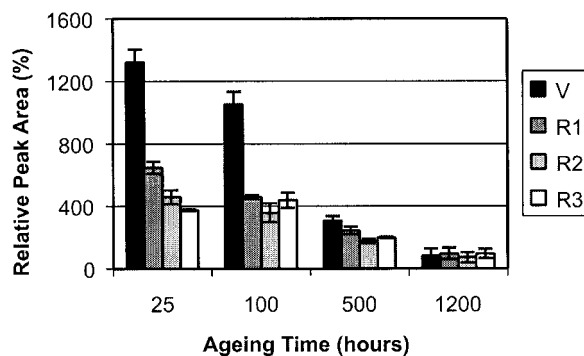


Figure 7 Relative peak area of 2-cyclopentyl-cyclopentanone extracted from virgin and recycled polyamide 6,6 after 25, 100, 500, and 1200 h of thermooxidation at 100°C.

pentanone, increased as a function of repeated recycling, whereas the amount of 2-cyclopentyl-cyclopentanone, the most abundant of the cyclopentanones, was lower in the recycled samples. After 25 h of aging, approximately twice as much 2-cyclopentyl-cyclopentanone was detected in the virgin material than in the material recycled once. 2-Cyclopentyl-cyclopentanone was probably formed already during polymerization, and it was then further degraded to cyclopentanone and other cyclopentanone derivatives during processing. This would explain the decrease in the amount of 2-cyclopentyl-cyclopentanone and the simultaneous increase in the other cyclopentanone derivatives during repeated processing. The lower molecular mass cyclopentanones can also be formed by thermal degradation of the polyamide during extrusion, as cyclopentanone and substituted cyclopentanones have earlier been identified as thermal degradation products of polyamide 6,6; that is, they are formed under conditions similar to those during extrusion.^{11–15}

Matrix changes caused by recycling and thermooxidation

From a visual examination of the samples during oxidation, it was evident that the yellowing of poly-

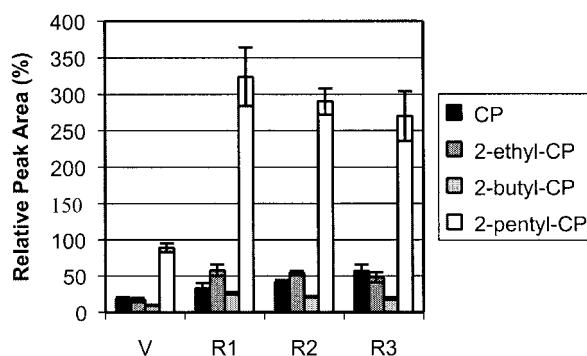


Figure 8 Relative peak areas of cyclopentanone and cyclopentanone derivatives extracted from virgin and recycled polyamide 6,6 after 25 h of thermooxidation at 100°C.

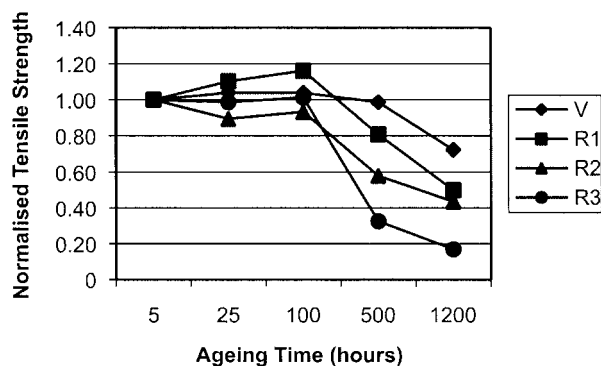


Figure 9 Loss of tensile strength of virgin and recycled polyamide 6,6 during 1200 h of thermooxidation at 100°C.

amide 6,6 recycled three times was more severe than the yellowing of polyamide 6,6 recycled twice. The increased susceptibility toward thermooxidation due to repeated processing was also monitored through the matrix changes, that is, the changes in the mechanical, thermal, and chemical properties during aging. Figure 9 shows the reduction in tensile strength for the virgin and recycled samples. The measured tensile strengths are shown normalized to the tensile strength after 5 h of oxidation to eliminate eventual moisture present in the samples before oxidation. Recycled materials showed a shorter induction period toward oxidation than virgin material; that is, their tensile strengths were affected by thermooxidation earlier than the tensile strength of the virgin material. A significant deterioration in tensile strength was noticed already after 100 h for the recycled materials, whereas the virgin material remained unaffected for the first 500 h. Furthermore, a larger decrease in the tensile strength was seen for recycled polyamide 6,6 than for virgin polyamide 6,6. After 1200 h, the virgin material retained 75% of its original tensile strength, whereas only 50, 40, and 20% of the original tensile strength remained for the samples recycled once, twice, and three times, respectively. All samples except R2 showed a small increase in tensile strength at early stages of oxidation. This was caused by the formation of a small amount of crosslinks in the material. Changes in the elongation at break and modulus of elasticity were also measured during aging, and the recycled materials showed a larger reduction in elasticity and more embrittlement than virgin materials.

DSC did not show any significant differences in the crystallinity of the recycled or thermooxidized samples. However, as shown in Figure 10, the melt peak temperature of polyamide 6,6 decreased because of oxidation. This reduction was larger for recycled polyamide 6,6 than for virgin material. However, the repeated recycling had no additional influence on the melt peak temperatures.

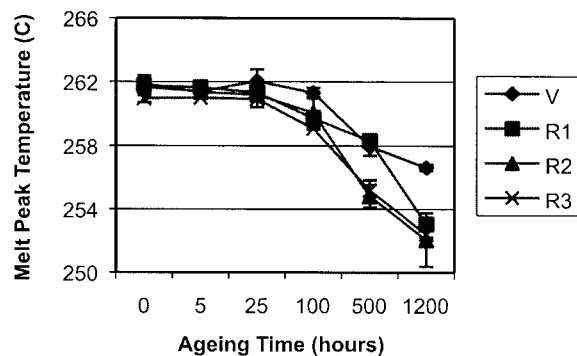


Figure 10 Melt peak temperatures of virgin and recycled polyamide 6,6 during 1200 h of thermooxidation at 100°C.

Carbonyl groups on the surfaces of the samples were monitored during oxidation with FTIR. After 1200 h of oxidation, more carbonyl groups were monitored on the surfaces of the samples recycled three times than on the surfaces of the other samples, as shown in Figure 11. However, approximately the same amounts of carbonyl groups were detected on the surfaces of the virgin material and the materials recycled once or twice. Measuring the increase in carbonyl groups with FTIR is a rather straightforward technique for monitoring oxidation and is commonly employed in the study of the oxidation of polyolefins. However, the large number of carbonyl groups already present in the polyamide backbone makes it difficult to measure the rather small increase in carbonyl groups due to oxidation.

Correlation of degradation product patterns to changes in mechanical properties

There was a good correlation between the recorded degradation product pattern and the changes in mechanical properties during the thermooxidation. Figure 12 shows the tensile strength and the amount of the most abundant thermooxidation product, 1-pentyl-2,5-pyrrolidinedione, as a function of the ther-

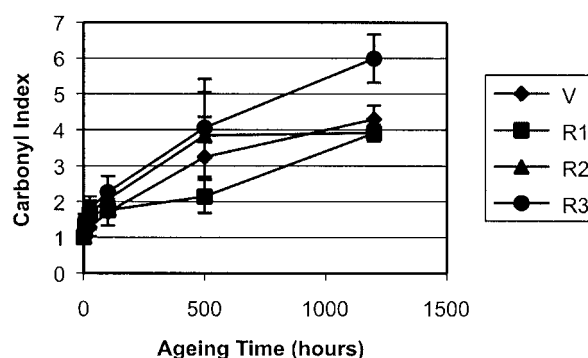


Figure 11 Relative amounts of carbonyl groups at 1716 cm^{-1} on the surface of virgin and recycled polyamide 6,6 during thermooxidation at 100°C as measured by FTIR.

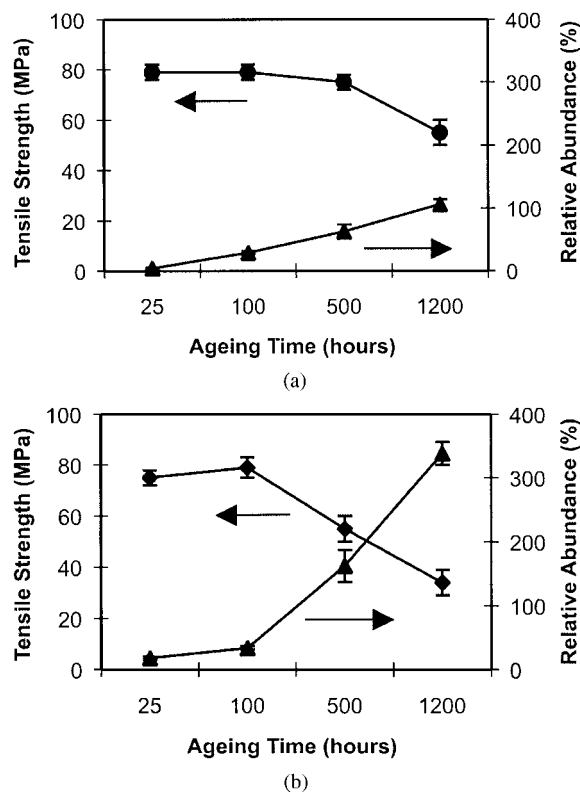


Figure 12 Loss of tensile strength versus the formation of 1-pentyl-2,5-pyrrolidinedione during 1200 h of thermooxidation of (a) virgin and (b) once recycled polyamide 6,6 at 100°C.

mooxidation time for the virgin material and the material recycled once. Longer oxidation times were required to detect changes in the tensile strength, whereas differences in the degradation product patterns could already be seen during the first 100 h with HS-SPME/GC-MS. When the induction period was surpassed, the tensile strength of polyamide 6,6 decreased rapidly. At the same time, a large amount of 1-pentyl-2,5-pyrrolidinedione was formed in the material. Also, the number and amount of the other thermooxidation products increased simultaneously in the recycled samples, and a large number of chain fragments were formed between 100 and 500 h of oxidation; this coincided with the rapid decrease in mechanical properties.

DSC, FTIR, and mechanical testing are well-established techniques for characterizing polymers, and they have earlier been applied successfully to studies of the thermooxidative degradation of polyamide 6,6.^{1,2,21} GC-MS has earlier been used to identify different low-molecular-mass compounds extracted from polymers.^{22–30} The increased susceptibility of recycled polyamide 6,6 toward oxidation was shown by all four methods employed. However, only HS-SPME/GC-MS and tensile testing were able to differentiate between the samples recycled one, two, or three times.

HS-SPME/GC-MS showed that the amounts of degradation products increased with the number of extrusions. FTIR and DSC measurements did not provide sufficiently clear and evident data to differentiate between samples recycled for different times.

CONCLUSIONS

A good correlation between mechanical properties and degradation product patterns was observed. The analysis of the degradation product pattern also gives, therefore, information about the status of the polymer matrix, and the correlation could be used to develop better quality-control tests for recycled materials. The rapid decrease in tensile strength after the induction period coincided with the increasing number and amount of degradation products formed. The usefulness of GS-MS, combined with the sensitive SPME technique as a characterizing tool, was demonstrated, as it was the most sensitive method for tracking degradation at early stages of thermooxidation. HS-SPME/GC-MS was also the technique that most clearly showed differences between virgin and recycled materials, revealing the increased formation of degradation products in recycled polyamide 6,6. The induction period during oxidation was shorter for the recycled materials than for the virgin material. A rapid decrease in tensile strength was observed between 100 and 500 h for the materials recycled one, two, or three times. The tensile strength of the virgin material, however, remained almost constant until 500 h. The identified degradation products could be divided into four groups: cyclic imides, pyridines, chain fragments, and cyclopentanones. After 1200 h at 100°C, 1-pentyl-2,5-pyrrolidinedione was the most abundant degradation product in both virgin and recycled polyamide 6,6. Large amounts of cyclopentanone derivatives were extracted from the unaged material. The amounts of cyclopentanones, however, decreased during thermooxidation. The cyclopentanones were, therefore, not thermooxidation products.

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References

1. Eriksson, P. A.; Boydell, P.; Eriksson, K.; Månson, J. A. E.; Albertsson, A.-C. *J Appl Polym Sci* 1997, 65, 1619.
2. Eriksson, P. A.; Boydell, P.; Månson, J. A. E.; Albertsson, A.-C. *J Appl Polym Sci* 1997, 65, 1631.
3. Karstens, T.; Rossbach, V. *Makromol Chem* 1989, 190, 3033.
4. Karstens, T.; Rossbach, V. *Makromol Chem* 1990, 191, 757.
5. Do, C. H.; Pearce, E. M.; Bulkin, B. J.; Reimschuessel, H. K. *J Polym Sci Part A: Polym Chem* 1987, 25, 2301.
6. Fromageot, D.; Roger, A.; Lemaire, J. *Angew Makromol Chem* 1989, 170, 71.

7. Gijsman, P.; Tummers, D.; Janssen, K. *Polym Degrad Stab* 1995, 49, 121.
8. Thanki, P. N.; Singh, R. P. *Polymer* 1998, 39, 6363.
9. Sharkey, W. H.; Mochel, W. E. *J Am Chem Soc* 1959, 81, 3000.
10. Do, C. H.; Pearce, E. M.; Bulkin, B. J.; Reimschuessel, H. K. *J Polym Sci Part A: Polym Chem* 1987, 25, 2409.
11. Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* 1987, 20, 2991.
12. Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Impallomeni, G.; Montaudo, G. *Polym Degrad Stab* 1988, 23, 25.
13. Soto-Valdez, H.; Gramshaw, J. W. *J Mater Sci Lett* 2000, 19, 823.
14. MacKerron, D. H.; Gordon, R. P. *Polym Degrad Stab* 1985, 12, 277.
15. Conway, D. C.; Marak, R. *J Polym Sci Polym Chem Ed* 1982, 20, 1765.
16. Lomakin, S. M.; Artsis, M. I.; Zaikov, G. E. *Int J Polym Mater* 1994, 6, 187.
17. Ohtani, H.; Nagaya, T.; Sugimura, Y.; Tsuge, S. *J Anal Appl Pyrolysis* 1982, 4, 117.
18. Gröning, M.; Hakkarainen, M. *J Chromatogr A* 2001, 932, 1.
19. Matsui, H.; Arrivo, S. M.; Valentini, J. J.; Weber, J. N. *Macromolecules* 2000, 33, 5655.
20. Lánská, B.; Makarov, G. G.; Sebenda, J. *Angew Makromol Chem* 1992, 196, 143.
21. Eriksson, P. A.; Albertsson, A.-C.; Eriksson, K.; Månson, J. A. E. *J Therm Anal Calorim* 1998, 53, 19.
22. Hakkarainen, M.; Albertsson, A.-C.; Karlsson, S. *J Chromatogr A* 1996, 741, 251.
23. Hakkarainen, M.; Albertsson, A.-C.; Karlsson, S. *J Environ Polym Degrad* 1997, 5, 67.
24. Hakkarainen, M.; Karlsson, S.; Albertsson, A.-C. *J Appl Polym Sci* 2000, 76, 228.
25. Hakkarainen, M.; Karlsson, S.; Albertsson, A.-C. *Polymer* 2000, 41, 2331.
26. Karlsson, S.; Hakkarainen, M.; Albertsson, A.-C. *J Chromatogr A* 1994, 688, 251.
27. Karlsson, S.; Hakkarainen, M.; Albertsson, A.-C. *Macromolecules* 1997, 30, 7721.
28. Khabbaz, F.; Albertsson, A.-C.; Karlsson, S. *Polym Degrad Stab* 1998, 61, 329.
29. Khabbaz, F.; Albertsson, A.-C.; Karlsson, S. *Polym Degrad Stab* 1999, 63, 127.
30. Khabbaz, F.; Albertsson, A.-C. *Biomacromolecules* 2000, 1, 665.