

Effect of Thermal-Oxidative Aging on Mechanical, Chemical, and Thermal Properties of Recycled Polyamide 66

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Received 27 November 1996; accepted 23 January 1997

ABSTRACT: This article addresses the effect of thermal aging on unreinforced and glass-reinforced recycled polyamide 66. As an accelerated test, injection-molded test bars were aged at 110, 140, and 170°C for up to 4000 h in air to simulate service life. FTIR spectroscopy demonstrated that the oxidative degradation primarily occurred between the surface and a depth of 0.5 mm. Furthermore, the degradation in the surface region was more pronounced with recycled as well as unstabilized materials. Reprocessing resulted in a faster increase of carbonyl groups, a decrease in melting peak temperature, and elongation at break during subsequent aging. Because of process-induced fiber shortening, however, the elongation at break of recycled reinforced samples was always at least as high as that of virgin samples for up to 4000 h of aging at 140°C. The decrease in melting peak temperature as determined by differential scanning calorimetry (DSC) indicated that the surface or boundary regions of the crystallites in the material are affected by aging. The loss in elongation at break for the reinforced material was shown to correlate with the reduction in melting peak temperature of material taken from the surface region of aged samples. The contribution of the degraded surface region to the properties was studied by removal of surface layers prior to testing. The degradation in the surface region was the sole cause, even of glass fiber-reinforced polyamide, for the embrittlement of aged samples. Furthermore, aging-induced changes in tensile strength and modulus were independent of the removal of the surface region, indicating that these properties are controlled by changes occurring in the bulk of the material. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1619–1630, 1997

Key words: polyamide 66; recycling; heat resistance in an oxidative environment; DSC; FTIR spectroscopy

INTRODUCTION

Glass-fiber-reinforced plastics have been widely used in various environments because of their ex-

cellent properties. Short-fiber-reinforced polyamide 66 is commonly used in automotive applications. Recycling of plastics is now a major concern in the automotive industry. Rising waste-handling costs and environmental regulations related to plastics disposal are strong driving forces towards a greater degree of in-plant recycling and recycling of postconsumer waste. Nevertheless,

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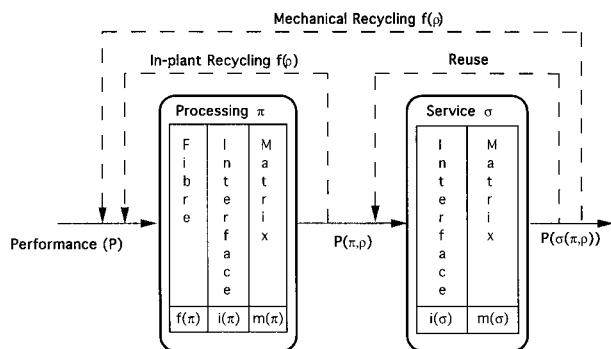


Figure 1 Schematic illustration of process-induced and service-induced degradation of the individual phases of glass-fiber-reinforced thermoplastics.

only small quantities of polyamides are currently recycled for engineering applications.

Process-induced degradation during the recycling operation may affect the durability and the reliability of reprocessed materials. Thus, it is important to investigate the interaction between process-induced degradation and the magnitude of degradation during subsequent service. Figure 1 is a schematic illustration of process-induced and service-induced degradation on the individual composite components of glass-fiber-reinforced thermoplastics. Before any critical recycling can take place, it is important to determine which factors or degradation mechanisms [$m(\pi)$, $i(\pi)$], $f(\pi)$, $f(\rho)$, $m(\sigma)$, $i(\sigma)$], as defined in Figure 1, control the performance or durability $\{P[\sigma(\pi, \rho)]\}$ of recycled materials.

Previous studies on heat-stabilized glass-fiber-reinforced polyamide 66 showed that in-plant recycling at a 100% regrind level decreases the mechanical performance by about 10% compared with virgin samples.¹ Furthermore, it was shown that the decrease in tensile strength of reprocessed samples is strongly related to process-induced fiber shortening $f(\pi, \rho)$. Thus, the influence of reprocessing on the short-term mechanical performance of the matrix $m(\pi)$ and the fiber–matrix interface $i(\pi)$ for this resin was limited. In contrast, the thermal-oxidative stability of the matrix measured by differential scanning calorimetry (DSC) decreased as a function of in-plant recycling.² The decreased matrix stability suggests that the recycled material, unless restabilized, will experience higher deterioration rates during subsequent service or accelerated thermal aging.

Many publications on the thermal-oxidative degradation of polyamide 66 that address a wide

variety of changes occurring in the material during the degradation process are available. A good review of the literature concerning this subject is given by Karstens and Rossbach.³ It is well known that exposure of polyamides to an oxidative environment causes changes in their physical, chemical, and mechanical characteristics.^{4–10} The literature (4–10) addresses changes in calorimetric behavior,^{4,5} infrared (IR) absorption bands,^{6–8} and mechanical properties.^{8–10} It is also known that the surface region of a thermally aged polyamide material will undergo more severe degradation than the interior.^{9,11} Molecular weight determination^{9,11} showed that the molecular weight of samples from the surface of aged specimens decreased considerably, whereas samples from the bulk of embrittled specimens increased, decreased, or remained constant according to the aging conditions. Harding and MacNulty⁹ concluded that the oxidation reaction prevails on the surface, but a condensation reaction takes place simultaneously in the interior. Valko and Chiklis¹⁰ showed that the molecular weight decreases on heating in the presence of air but increases on heating in the presence of antioxidants or in a nitrogen atmosphere. They suggested that action of oxygen causes chain scission, but heat alone causes the material to crosslink. Pavlov et al.¹¹ reported that the molecular weight decreases most rapidly in the surface layers of polyamide 6, whereas the molecular weight increases in the layers more than 0.3 mm from the surface. Their results further indicate the possibility of competition between chain scission and polycondensation processes in the surface layers.

This article discusses experiments conducted to investigate what controls the durability of recycled polyamide 66 relative to virgin material and to explore the interaction between process-induced and subsequent service-related degradation. To study the difference between virgin material and in-plant recycled material, and to determine which factors control durability $P[\sigma(\pi, \rho)]$, injection-molded test samples were aged in air at elevated temperatures as an accelerated test condition to simulate service life. Additionally, the influence of different important factors, such as aging time, temperature, and heat stabilization, were investigated.

The mechanical performance was characterized by tensile tests. The degradation of the matrix during thermal aging was investigated by Fourier transform infrared (FTIR) spectroscopy and DSC. FTIR spectroscopy was used to follow

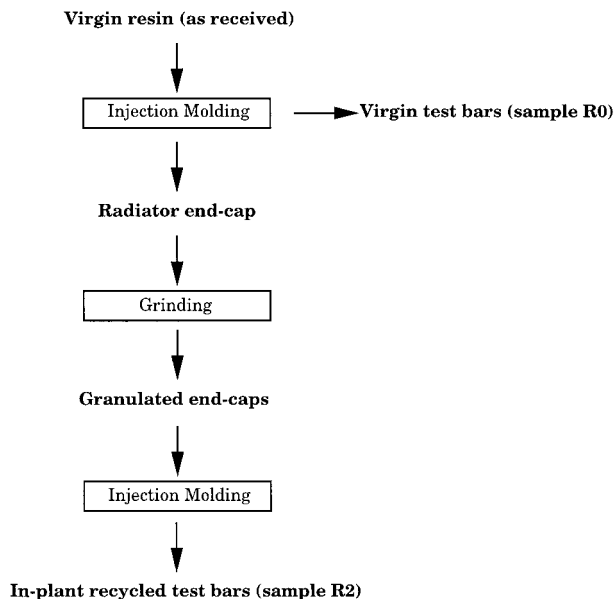


Figure 2 Processes used to prepare glass-fiber-reinforced samples R0 (virgin material) and R2 (100% in-plant regrind).

changes in the intensities of IR absorption bands in the 1800–1650 cm^{-1} region that are related to carbonyl groups. DSC was used to monitor changes in the degree of crystallinity and melting peak temperature over the aging period.

EXPERIMENTAL

The test samples were injection-molded from commercial polyamide 66. Both unreinforced resin and material reinforced with 30 wt % of short glass fibers were investigated.

Two different grades of unreinforced polyamide 66 were used: neat (DuPont Zytel EFE 1032) and heat-stabilized (DuPont Zytel 103 HSL). To characterize the influence of reprocessing, unstabilized pellets were reextruded before injection molding. Standard tensile bars according to ISO 527 specifications were supplied by DuPont.

Glass-fiber-reinforced test samples were processed from heat-stabilized polyamide 66 (DuPont Zytel EFE 7185 BK99). To characterize the influence of in-plant recycling, samples were processed according to two different schedules. First, virgin samples were injection molded from virgin resin. Second, recycled samples were obtained from virgin material by the following operations: (1) injection molding into radiator end-caps, (2) granulating, and (3) injection molding into test bars containing 100% regrind, as shown in Figure 2.

Radiator end-caps were ground using a Rapid granulator 3026-C with a tip speed of 10 m/s and an output of up to 200 kg/h. The granulator was equipped with three rotating knives and two twin-edge reversible fixed knives. Test specimens were injection molded using a Demag D60-182 injection molding machine with a maximum injection capacity of 97 cm^3/s and a screw diameter of 32 mm. The material straight from bags was dried for 4 h at 80°C before the injection molding. The processing parameters are reported in Table I.

Injection-molded test bars were aged in air at elevated temperatures as an accelerated test condition. The thermal aging was performed using conventional air circulating ovens. Unreinforced samples were aged at temperatures of 110, 140, and 170°C for 4, 20, 100, and 500 h. Glass-fiber-reinforced samples were aged at 140°C for up to 4000 h.

All examined samples are reported in Table II. Tensile tests of unreinforced samples, except for sample S3, were performed on dry as-molded bars. Before tensile tests of reinforced samples and sample S3, the specimens were held in 50% relative humidity (RH) at 80°C until equilibrium was reached. For calorimetric (DSC) and FTIR spectroscopic analysis, the samples were dried to equilibrium in a vacuum oven before testing.

Tensile tests were performed with two different types of test bars. Tensile tests of unreinforced samples (S0–S3) were performed according to ISO 527. Tests of glass-fiber-reinforced samples (R0 and R2) were performed according to ASTM D-638M specifications. The testing was carried out in air at 23°C and 50% RH.

FTIR analysis was performed to study the formation of carbonyl groups in unreinforced mate-

Table I Injection Molding Variables of Reinforced Samples R0 and R2

Processing Parameters	
Mold temperature (°C)	110
Barrel temperature (°C)	275–290
Melt temperature (°C)	290
Injection time (s)	0.7
Holding time (s)	6
Cooling time (s)	10
Total cycle time (s)	21
Screw speed (rpm)	190
Injection speed (cm^3/s)	37
Back pressure (MPa)	7.5
Hold pressure (MPa)	50

Table II Samples Examined

Samples	S0	S1	S2	S3	R0	R2
Grade	Zytel EFE 1032	Zytel EFE 1032	Zytel 103 HSL	Zytel EFE 1032	Zytel EFE 7185 BK99	Zytel EFE 7185 BK99
Heat-stabilized	No	No	Yes	No	Yes	Yes
Glass-fiber-reinforced	No	No	No	No	Yes	Yes
Moisture condition during mechanical testing	Dry	Dry	Dry	Eq. 50% r.h.	Eq. 50% r.h.	Eq. 50% r.h.
% regrind	0	100	0	0	0	100
Tensile bars	ISO 527	ISO 527	ISO 527	ISO 527	ASTM D638M	ASTM D638M
Aging temperatures (°C)	110/140/170	110/140/170	110/140/170	140	140	140
Aging times (h)	4/20/100/500	4/20/100/500	4/20/100/500	20	500/1000/2000/3000/4000	500/1000/2000/3000/4000

rial. The measurements were made with a Perkin–Elmer FTIR Spectrometer 1760 X using the attenuated total reflection technique (ATR). The instrument was equipped with a micro ATR holder and a KRS-5 prism (Spectratech, Inc.) having an incident angle of 45° and a refractive index of 2.37. Samples of 0.05 mm thickness were microtomed from injection-molded tensile bars at different distances from the surface. Each spectrum was based on 20 scans, and the intensity in the carbonyl region ($\approx 1730 \text{ cm}^{-1}$) was studied by using the $\approx 1200 \text{ cm}^{-1}$ band assigned to amide III mode + $\gamma w(\text{CH}_2) + \gamma t(\text{CH}_2)$ as an internal standard.¹²

Calorimetric analysis of unreinforced samples was carried out in a TA Instruments thermal analyzer equipped with a 910 DSC module. Samples, consisting of six microtomed sections of 0.05 mm thickness, weighed $3.5 \pm 0.5 \text{ mg}$. The samples were taken at different distances from the surface of test bars. Analysis of reinforced samples was carried out in a Mettler DSC 820. Samples of 0.2 mm thickness, weighing $5.0 \pm 0.5 \text{ mg}$, were microtomed from the surface and from the bulk of molded test bars. During operation, the instruments were purged with a constant flow of nitrogen of 4 l/h. Melting thermograms were recorded on samples heated at a rate of $10^\circ\text{C}/\text{min}$ from 50 to 285°C . The melting peak temperature and degree of mass crystallinity (ω_c) were determined, the latter according to the equation

$$\omega_c = \frac{\Delta h}{\Delta h^\circ(1 - w_f)}$$

where w_f is the weight fraction of fibers, Δh is the heat of fusion for the sample, and Δh° is the heat of fusion for 100% crystalline material, which has a value for polyamide 66 equal to $196 \text{ kJ}/\text{kg}$.¹³ Aged material exhibited one weak low melting peak temperature and one intensive high melting peak temperature. The reported data correspond to the high peak temperature.

RESULTS AND DISCUSSION

Thermal Aging of Unreinforced Polyamide 66

Degradation of polymers during service or accelerated aging is influenced by environment, temperature, part thickness, reprocessing, stabilization, and so forth. In this section, the influence of thermal aging on surface characteristics of reextruded

Table III Elongation at Break of Samples S0–S2 (Dry)

Aging Temperature (°C)	Aging Time (h)	Elongation at Break (%)		
		Sample S0	Sample S1	Sample S2
—	—	79	56	32
110	4	58	49	40
	20	55	34	35
	100	51	40	33
	500	1.1	1.3	37
140	4	41	36	38
	20	41	11.4	33
	100	1.3	1.5	41
	500	—	—	1.0
170	4	2.4	2.3	40
	20	—	—	39
	100	—	—	38

and of heat-stabilized unreinforced polyamide 66 is presented and discussed.

Mechanical Properties

One important characteristic of polyamides is the effect of moisture content on their mechanical properties.¹⁴ The effect of thermal aging on the elongation at break of dry samples S0–S2 is reported in Table III. Three characteristic features may be extracted from these results:

1. Comparison between unaged samples shows that addition of the heat stabilizer decreases the elongation by about 60%. Reextrusion of unstabilized samples before injection molding results in a 30% decrease.
2. Exposure of unstabilized polyamide 66 (S0 and S1) to air at elevated temperatures results in a severe reduction of the elongation. This was already observed after 4 h of aging at all investigated temperatures.
3. Addition of heat stabilizers (S2) substantially improves the resistance to subsequent thermal aging. After 4 h of aging, the elongation at break manifests an increase at all investigated temperatures. Furthermore, the elongation exhibits higher values, compared with unaged samples, up to 500 h of aging at a temperature of 110°C and up to 100 h of aging at 140 and 170°C.

The determined elongation at break of unreinforced polyamides showed that prolonged exposure to an oxidative environment induces embrittlement. Furthermore, the results confirmed that

addition of heat stabilizers substantially improves the resistance to thermal-oxidative degradation.¹⁵ In addition to suppressed thermal degradation by heat stabilization, the observed increase in elongation at break may be attributed to an annealing effect, since the samples were aged above the glass transition temperature (T_g).¹³ This factor may result in the release of possible internal stresses induced during processing. The microstructural mechanisms that occur during annealing are thought to be chain rearrangements caused by hydrogen bond rupture, relaxation of the load-bearing taut-tie molecules, and increased chain motion.¹⁶

Surface Characteristics

It is known that the surface area of an aged polyamide 66 material will undergo more severe degradation than the interior.⁹ To confirm this, test bars of unstabilized unreinforced polyamide 66 (S3) were thermally aged for 20 h at 140°C. The contribution of the degraded surface region to the elongation at break was studied by removal of surface layers. A 0.5-mm thick surface region was milled away from the test bars, which were equilibrated at 50% RH, prior to tensile testing. The results are reported in Table IV.

The effect of thermal aging on the surface region is illustrated by the comparison of elongation at break between unmilled and surface-milled samples. The aged unmilled sample showed a significant decrease compared with the unaged sample. For samples with a removed surface region, the elongation was determined to be more than 100% for both unaged and aged samples. These

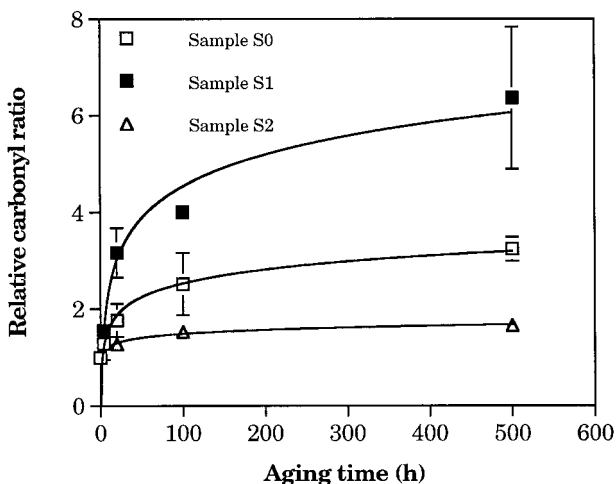
Table IV Elongation at Break of Sample S3 (50% RH)

Aging Condition	Removed Surface Region	Elongation at Break (%)
Unaged	No	> 100
140°C/20 h	No	7.1
Unaged	Yes	> 100
140°C/20 h	Yes	> 100

results confirm that the degradation in the surface region is responsible for the embrittlement of aged samples and, thus, may control the tensile properties.

Previous FTIR spectroscopic studies on polyamides have shown that the intensities of IR absorption bands in the 1800–1650 cm^{-1} region, which are related to carbonyl groups formed during thermal-oxidative or photooxidative degradation, change with time and temperature.^{6–8} The growth of these absorption bands was interpreted as resulting from (1) formation of carbonyl groups such as aldehydes, carboxylic acids, and ketones; (2) different degrees of hydrogen bonding; (3) different conformations of the carbonyl groups; and (4) their temperature dependence.⁶

Through FTIR spectroscopy we have demonstrated that aged samples exhibit a considerable growth of the absorption bands in the carbonyl region. The influence of aging at 110°C on carbonyl formation in the surface of unreinforced samples S0–S2 is illustrated in Figure 3. The rel-

**Figure 3** Relative carbonyl ratio at the surfaces of unreinforced samples S0–S2 as a function of aging at 110°C.**Table V** Thermal Characteristics of the Surface of Sample S2 During Thermal Aging at 100°C

Aging Time at 110°C (h)	Melting Peak Temperature (°C)	Mass Crystallinity (%)
Unaged	260.0	36.0
20	259.5	36.0
100	259.1	36.7
500	257.8	35.8

ative carbonyl ratio $A(1730 \text{ cm}^{-1})/A(1200 \text{ cm}^{-1})$, normalized with respect to unaged samples, is shown as a function of aging time.

The carbonyl ratio increases as a result of thermal aging, and the changes are attributed to thermal-oxidative degradation. Reextruded samples (S1) exhibit the largest increases, whereas in heat-stabilized samples (S2) only slight increases were observed, indicating that the degradation was almost prevented. It is also observed that the initial stages of the thermal aging had a stronger influence on the increase of the carbonyl ratio.

Calorimetric analysis (DSC) was used to monitor changes over the aging period. The degree of crystallinity and the melting peak temperature for samples cut from superficial layers of heat-stabilized tensile bars (S2) aged at 110°C are reported in Table V.

The crystallinity manifested no significant changes during aging, whereas the melting peak temperature was found to decrease. Oxidation in semicrystalline polymers is generally known to occur in the amorphous regions. However, the results not only indicate that the material in the surface region of tensile bars is affected by oxidative degradation but that the crystalline regions are also affected. It is known that the core of crystallites is inert to oxidation, but their surfaces and boundary regions could well be oxidized (e.g., scission of the tie-chains between the crystallites).¹⁷ On the basis of the results, it is suggested that the decrease in melting peak temperature is due to less-ordered crystallites in aged material (i.e., an oxidation-induced increase in surface energy of the crystallites).

Figure 4 presents profiles through thickness of the relative carbonyl ratio as a function of distance from surface for heat-stabilized samples (S2). The ratio was normalized with respect to unaged samples at a distance of about 1 mm from the surface. An increased carbonyl ratio was observed in the surface after 100 h of thermal aging

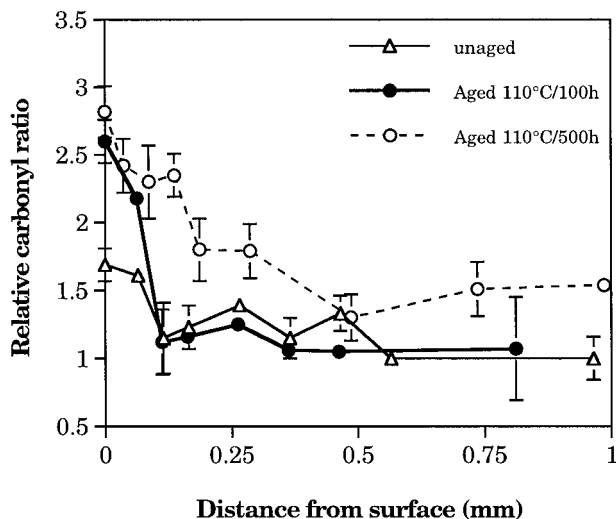


Figure 4 Relative carbonyl ratio as a function of distance from surface for sample S2 (heat-stabilized) after aging at 110°C.

at 110°C, relative to the unaged sample. The results show that the carbonyl ratio increased within a depth of about 0.1 mm from the surface. By contrast, no changes were observed in the interior of the sample.

The results indicate, as shown elsewhere for polyolefins,^{18,19} that the rate of absorption of air through sample thickness controls the oxidative degradation. During aging it is common to observe diffusion-limited oxidation through the thickness of polymers. This phenomenon occurs when the consumption rate of oxygen in the material is greater than the rate at which oxygen can be resupplied from the atmosphere by diffusion processes.²⁰ As can be seen in Figures 3 and 4, the carbonyl ratio exhibits more or less the same value at the surface after 500 h of aging as after 100 h. On the other hand, the thickness of the oxidatively degraded region shows an increase, between 100 and 500 h, from about 0.1 to 0.5 mm.

The presented results also indicate that thermal-oxidative degradation exhibits a strong position dependence, starting at the surface and then propagating inwards; moreover, the carbonyl ratio gives information about the thickness of the oxidized layer. It has also been noted from unpublished data that an increased aging temperature results in a raised carbonyl ratio in the surface and in a reduced thickness of the affected layer.

Heat Stabilization

The influence of heat stabilization is illustrated in Figure 5, which shows the relative carbonyl

ratio $A(1730\text{ cm}^{-1})/A(1200\text{ cm}^{-1})$ as a function of distance from the surface after 500 h of aging at 110°C.

The unstabilized polyamide (S0), which was very brittle in the surface region, shows a more developed degradation profile compared with the heat-stabilized sample (S2). The results indicate that thermal-oxidative degradation occurs primarily within a depth of 0.5 mm from the surface. Furthermore, the degradation in this surface region seems to strongly influence the mechanical properties. As seen in Table III, there is a distinct difference in elongation at break between unstabilized (S0) and heat-stabilized samples (S2) after 500 h of thermal aging at 110°C. The significant decrease in elongation at break of unstabilized samples may be explained by the degradation profile shown in Figure 5.

Figure 6 presents the melting peak temperature profiles of microtomed sections taken from samples S0 and S2 after 20 h of thermal aging at 140°C. For the unstabilized sample (S0), a decreased peak temperature was observed in a 0.1-mm thick region at the surface. An approximately 3°C overall decrease was observed compared with the bulk of the sample and with unaged samples (Table VI). The heat-stabilized sample (S2) shows a decreased melting temperature of about 1°C in a 0.35-mm thick region. The results imply, as mentioned earlier, less perfection for the crystalline regions in the surface layer of aged material than for aged bulk material or unaged material.

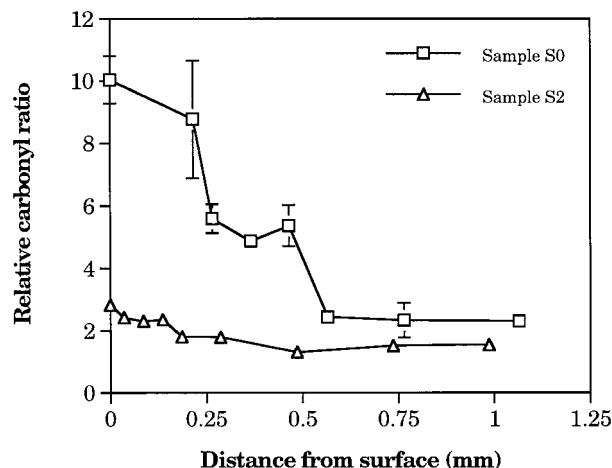


Figure 5 Relative carbonyl ratio for samples S0 (unstabilized) and S2 (heat-stabilized) as a function of distance from surface after 500 h of aging at 110°C.

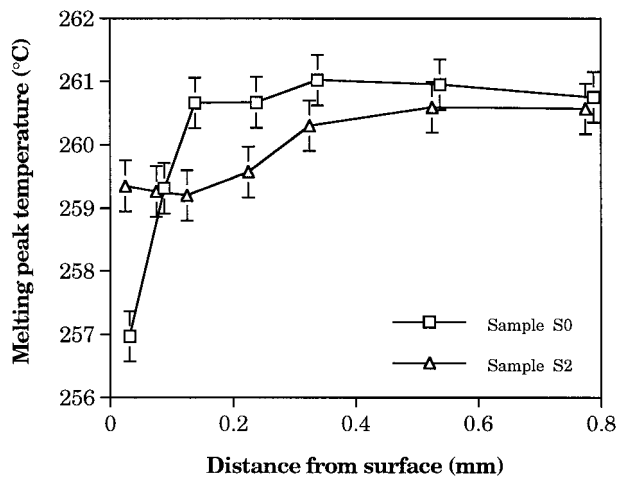


Figure 6 Melting peak temperature for samples S0 (unstabilized) and S2 (heat-stabilized) as a function of distance from surface after 20 h of aging at 140°C.

Reprocessing

The influence of aging on carbonyl formation in the sample surface is illustrated in Figure 3. The carbonyl ratio of aged samples S0 and S1 exhibits considerable growth. The reprocessed samples (S1) shows a more intense increase of the carbonyl ratio relative to virgin samples (S0). The influence of reprocessing and subsequent thermal aging on the relative carbonyl ratio through thickness is illustrated in Figure 7. The samples were aged for 20 h at 140°C.

The reprocessed sample (S1) exhibits a significantly higher carbonyl ratio in the surface region compared with the sample not reextruded (S0). In contrast, at a distance of about 0.1 mm from the surface the results suggest a similar or

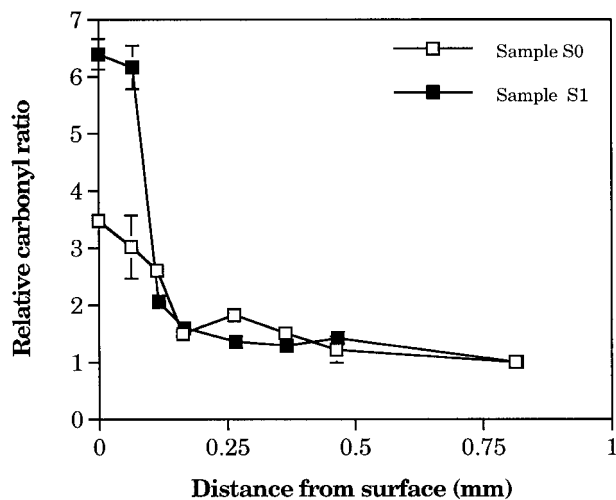


Figure 7 Relative carbonyl ratio for samples S0 (unstabilized) and S1 (unstabilized/reextruded) as a function of distance from surface after 20 h of aging at 140°C.

a higher ratio in the sample processed just once. Furthermore, the thickness of oxidized material was found to be about 0.4 mm for sample S0 and 0.25 mm for sample S1. The relatively thin layer of significantly oxidized material for the reextruded sample indicates that the degraded surface initially formed during subsequent thermal aging controls continued degradation through thickness. An intense degradation of the surface region may decrease the air diffusion rate and, thus, to some extent protect against and inhibit further degradation through the thickness.

Surface region characteristics recorded from DSC thermograms of samples S0 and S1 after thermal aging at 140°C are reported in Table VI. The melting peak temperature shows a decrease as a function of aging. The overall decrease was about ~6 and 10°C for samples S0 and S1, respectively. The degree of mass crystallinity was observed to increase for both samples. These results confirm, as described earlier, that degradation takes place in the material during aging and that the crystalline regions are affected.

Degradation profiles based on the carbonyl ratio and the results recorded from DSC thermograms indicate a more intense degradation of the surface region of reextruded samples. As can be seen in Table III, after 20 h of aging at 140°C the elongation at break decreases about 50% for sample S0, whereas the decrease is 80% for sample S1, compared with unaged samples. This difference may be explained by the results shown in

Table VI Thermal Characteristics of the Surface of Samples S0 and S1 During Thermal Aging at 140°C

Sample	Aging Time at 140°C (h)	Melting Peak Temperature (°C)	Mass Crystallinity (%)
S0	Unaged	260.3	37.4
	4	259.7	39.5
	20	257.0	41.9
	100	254.4	42.1
S1	Unaged	260.7	37.3
	4	258.1	40.2
	20	257.4	40.4
	100	250.9	51.9

Figure 7 indicating that the degradation in the outer surface region has a dramatic influence on the elongation at break.

To summarize, work on unreinforced polyamide 66 has confirmed that thermal aging causes changes in thermal, chemical, and mechanical characteristics. Thermal aging resulted in a raised carbonyl ratio, an increased degree of mass crystallinity, a decreased melting peak temperature, and in an induced embrittlement. The results show that the degradation exhibits a strong position dependence and that surface region controls deterioration in the elongation at break of aged polyamide. It can also be seen that heat stabilization substantially improves the resistance to degradation during thermal aging. Reextrusion before injection molding had a negative influence on the aging resistance. The degree of degradation in the outer surface region was more intense in reprocessed as well as in unstabilized samples. Furthermore, an intense degradation of the surface region resulted in a lower thickness of the affected surface layer.

Thermal Aging of Reinforced Polyamide 66

The influences of in-plant recycling and subsequent thermal aging on heat-stabilized glass-fiber-reinforced polyamide 66 were investigated as described in the following section. Injection-molded test bars were aged in air for up to 4000 h at 140°C. The aging was timed to achieve about a 50% reduction in elongation at break. The service lifetime of a polymer product at a specific temperature and in a specific environment is often defined as the time to a 50% decrease in an important property.

Mechanical Properties

The elongation at break of samples equilibrated at 50% RH containing virgin material (R0) and 100% in-plant regrind (R2) is shown as a function of aging time at 140°C in Figure 8. In the case of unaged samples, grinding and reprocessing resulted in an increased elongation at break. This change can be explained by a lessening of the restriction imposed by the fibers on the deformation of the matrix as a result of a reduced degree of fiber reinforcement in recycled samples.¹

During aging, the elongation at break decreased as a function of time. The recycled sample (R2) manifested a faster reduction compared with sample R0, indicating a more intense thermal-

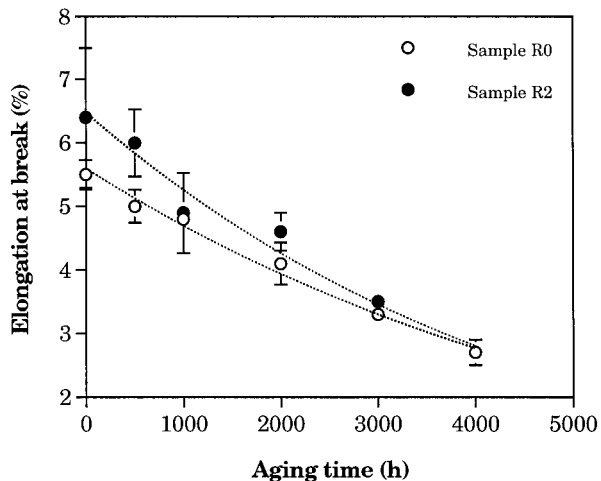


Figure 8 Elongation at break for samples R0 (virgin material) and R2 (100% in-plant regrind) as a function of aging time at 140°C (50% RH).

oxidative deterioration in the recycled material. Even though in-plant recycling shows a negative influence on aging resistance, the elongation at break of the recycled samples is always at least as high as for virgin samples. The changes induced by the recycling operation disappeared after about 4000 h of aging when both samples degraded to similar values of elongation at break. This observation can be explained by assuming that the degraded matrix controls the elongation at break regardless of the effect of reprocessing on the fiber length. Interestingly, the results suggest that the level of a 50% reduction, which is achieved after about 4000 h of aging for both samples, occurs in the time region where the elongation at break seems to be independent of in-plant recycling. Thus, the results demonstrate that the useful lifetime of 100% in-plant recycled samples fulfills the requirements on elongation at break of samples made from virgin material.

Thermal Properties

The influence of thermal aging at 140°C on the melting peak temperature (T_m) and the degree of crystallinity (ω_c) of the reinforced samples R0 and R2 is shown in Figure 9.

The studied material was taken from the surface region and from the bulk of test bars. The T_m in the bulk of the test bars showed essentially no change after 4000 h of aging relative to unaged test bars [Fig. 9(a)]. In contrast, the T_m in the superficial layers of the test bars was significantly affected by aging. After 4000 h of aging, the virgin

sample (R0) showed an approximately 7°C overall decrease compared with unaged samples, whereas the recycled sample (R2) showed a decrease of 9°C. The decrease is, as mentioned earlier, interpreted as being due to oxidative degradation.

In Figure 9(b), the ω_c is shown as a function of aging time. Both virgin and recycled material from the bulk of test bars manifested values after 4000 h of aging more or less similar to those for unaged material. The ω_c in the surface of the test bars was almost unaffected during the first 2000 h of aging. Between 2000 and 4000 h, however, both samples experienced an overall increase of about 6%. The observed changes in crystallinity during aging can not be used to confidently distinguish between samples containing virgin or recycled

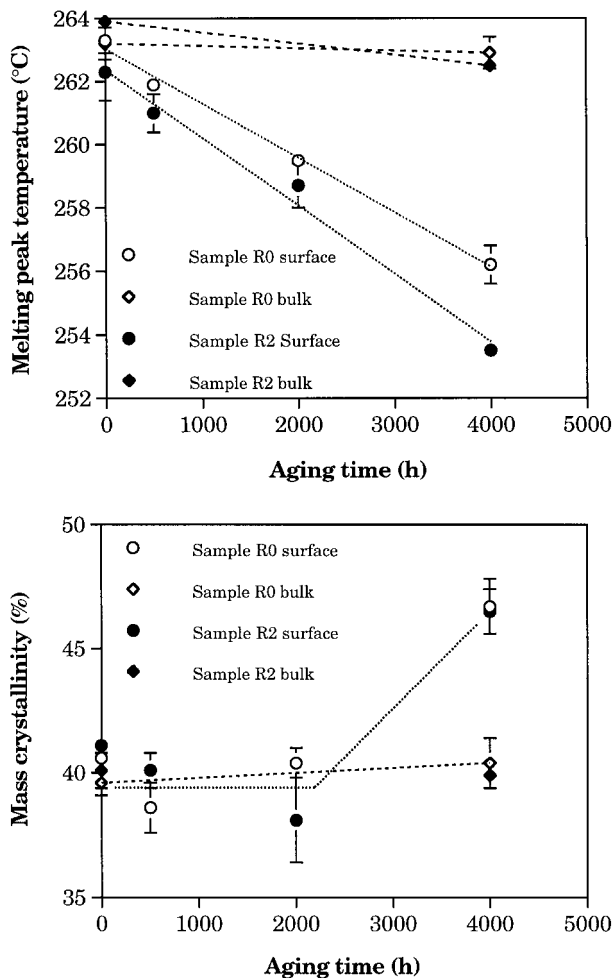


Figure 9 Influence of thermal aging at 140°C: (a) melting peak temperature; (b) mass crystallinity for samples R0 (virgin material) and R2 (100% in-plant regrind).

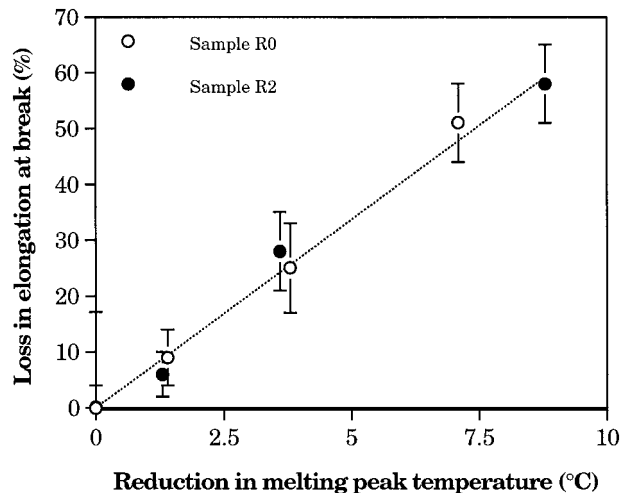


Figure 10 Loss in elongation at break for samples R0 (virgin material) and R2 (100% in-plant regrind) upon thermal aging at 140°C as a function of the reduction in melting peak temperature of material taken from the surface layer of test bars.

material. Nevertheless, the increase in crystallinity indicates that degradation takes place in the surface region of the material.

The reported results on reinforced polyamide 66 demonstrate that thermal aging causes changes in thermal and mechanical properties. In-plant recycling showed a negative influence on the rate of decline in elongation at break. However, after longer aging times, the results indicate that the oxidative degradation of the matrix is the dominant and controlling aspect, regardless of fiber-length reduction caused by reprocessing. DSC-data indicated that degradation takes place in the surface region, whereas material in the bulk of the test bars was negligibly influenced by aging.

In Figure 10, the elongation at break loss, relative to unaged samples, is plotted against the reduction in T_m of material taken from the surface region of test bars. Evidently, the deterioration in elongation at break during thermal aging correlates with the reduction in T_m at superficial layers of the test bars. These results indicate, as shown earlier for unreinforced material, that the loss in elongation at break is strongly related to changes of the matrix in the surface layer of the samples and that the crystalline regions of the material are affected.

Controlling Factor of Properties in Recycled Reinforced Polyamide 66

A 0.5-mm thick surface region was removed from unaged and aged (3000 h/140°C) tensile bars,

Table VII Tensile Properties Relative to Unaged Sample for Samples R0 (Virgin Material) and R2 (100% In-Plant Regrind)

Sample	Removed Surface Region	<i>E</i> -Modulus	Strength at Break	Elongation at Break
R0	no	1.17	1.11	0.62
R2	no	1.10	1.08	0.53
R0	yes	1.07	1.15	1.34
R2	yes	1.12	1.09	0.95

Properties measured after 3000 h of aging at 140°C (50% RH).

which were equilibrated at 50% RH before testing, made from virgin material (R0) and 100% in-plant regrind (R2). Tensile tests were performed before and after removal of the surface region. The recorded tensile properties after aging, as relative values to unaged samples, are reported in Table VII.

The effect of aging is illustrated by the samples with their original surface retained. Thermal aging of these samples resulted in a significant drop in elongation at break and in an increased tensile strength and modulus relative to unaged samples. The increased strength and modulus may be explained by a raised molecular weight induced through polycondensation in the interior of the samples.^{9,11} As expected, the relative elongation at break manifested a more pronounced decrease in the reprocessed sample (R2) compared with the virgin sample (R0). The recycled sample showed about a 50% decrease, whereas the virgin sample decreased 40%.

Samples with their surface region removed also displayed an increased relative tensile strength and modulus. For the recycled sample (R2), the relative elongation at break was close to unity (i.e., the elongation at break is more or less independent of aging). For the virgin sample (R0), the elongation at break was higher after the aging because of a higher degree of yielding prior to failure. These results confirm that the degradation in the surface region of fiber-reinforced polyamide 66 is responsible for the embrittlement of aged samples and that the surface degradation is more intense in in-plant recycled samples compared with virgin samples. Furthermore, the increase in tensile strength and modulus induced during aging seems to be independent of the removal of the surface region, indicating these properties are controlled by changes, most certainly an increased molecular weight, induced in the bulk of the test bars.

CONCLUSIONS

This article discussed the influence of thermal aging on unreinforced and glass-fiber-reinforced recycled polyamide 66 relative to virgin material. The results confirm that prolonged exposure to an oxidative environment at high temperatures causes changes in thermal, chemical, and mechanical characteristics. The degradation in the surface region of the test bars, which primarily occurred within a depth of 0.5 mm, was shown to be responsible for the embrittlement of aged material. It was also noted that the degree of degradation in the surface region was more pronounced with recycled as well as unstabilized samples.

Reextrusion before injection molding of unreinforced polyamide accelerated certain features during subsequent thermal aging. Reprocessed samples exhibited a faster increase in the formation of carbonyl groups and a decrease in melting peak temperature and elongation at break compared with virgin samples.

During aging of reinforced material, the in-plant recycled samples exhibited a faster reduction in elongation at break and melting peak temperature relative to virgin samples. In spite of this, the elongation at break of recycled samples was never lower than that of virgin samples for up to 4000 h of aging at 140°C. Furthermore, changes in tensile strength and modulus induced during aging were shown to be controlled by changes occurring in the bulk of the test bars.

The authors would like to thank the Swedish National Board for Industrial and Technical Development (NUTEK), DuPont de Nemours International S.A., and AB Konstruktions-Bakelit for their financial support and collaboration during this work.

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