

Effects of Reprocessing on the Structure and Mechanical Properties of Poly(trimethylene terephthalate)

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ABSTRACT: The effects of reprocessing by extrusion for up to four cycles on the structure and mechanical properties of poly(trimethylene terephthalate) (PTT) were studied. Reprocessing did not change the chemical structure of the polymer but led to both yellowing and molecular weight reduction. Young's modulus and the yield stress of PTT remained constant or decreased with successive extrusion cycles, probably because of the observed slight specific vol-

ume increase. The continuous reduction in the break properties due to reprocessing was smaller than that found in similar polyesters and was attributed to the molecular weight reduction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2775–2780, 2002

Key words: mechanical properties; poly(trimethylene terephthalate); recycling; degradation

INTRODUCTION

Polymer recycling is a common practice in the plastics industry for both environmental and economic reasons. In primary recycling, or reprocessing, single-component scrap plastics are transformed into new products with standard processing methods. The scrap can be used alone or, more often, is mixed with the virgin material at appropriate ratios according to the expected performance. However, the application of successive high-temperature/shear cycles during reprocessing can give rise to degradation. Degradation may appear in the form of both physical changes in the structure and chemical processes leading to chain scission, grafting, crosslinking, or unsaturation cyclization. These structural changes can lead to a loss in characteristics, such as appearance, chemical resistance, processability, and mechanical properties.¹

When degradation processes during melt processing are studied, the use of a high number of reprocessing cycles helps with the detection and determination of the nature of the degradation processes and also with the selection of an appropriate stabilizer. Moreover, the determination of the quantitative effects of reprocessing on the polymer properties can provide useful information about the processing conditions allowed for a minimum loss of properties and about the maximum amount of reprocessed material

that can be added to virgin material without an important reduction in a given property.

Studies on the nature of the degradation caused by reprocessing and its effects on the properties of polymers have been conducted for a large number of polymers, including polyethylene,² polypropylene,^{3–5} polycarbonate,^{6–8} poly(ethylene terephthalate) (PET),^{9–13} poly(butylene terephthalate) (PBT),¹⁴ nylon-6,¹⁵ poly(ether imide),¹⁶ poly(ether ether ketone),¹⁷ and liquid-crystalline polymers.^{18,19}

Poly(trimethylene terephthalate) (PTT) is a polymer that belongs to the aliphatic–aromatic polyester family, whose most used components are PET and PBT. PTT has only recently been commercialized. For this reason, it has been reported in only a few articles. Among these, studies of the thermal decomposition of PTT have been recently published.^{20,21} However, the effects of reprocessing on their structure and properties have not been reported.

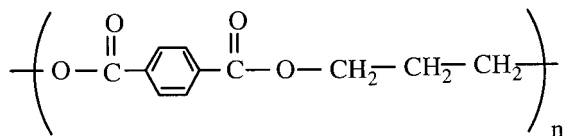
In this work, the effects of reprocessing by repeated extrusion on the structure and properties of PTT were studied. The polymer was always finally injection-molded to obtain specimens for the different characterization and testing techniques. The variations in the chemical and physical structural characteristics were analyzed, and the effects of these variations on the mechanical properties were determined with tensile and impact tests.

EXPERIMENTAL

The PTT used in this work (Corterra 509200) was kindly supplied by Shell Chemical Co. (Houston, TX). PTT has the following chemical structure:

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According to the recommendations of the manufacturer, the polymer was dried at 150°C for 4 h in an air oven before each processing cycle to minimize degradation reactions caused by moisture. Extrusion was carried out in a corotating twin-screw extruder mixer (Collin ZK-25, Ebersberg, Germany). The melt temperature was 270°C, and the screw speed was 30 rpm. After each extrusion cycle, the extrudate was pelletized and injection-molded in a Battenfeld BA-230E (Rottingbrunn, Austria) reciprocating screw injection-molding machine at a barrel temperature of 270°C and at a mold temperature of 21°C. The screw rotation rate was 140 rpm, the injection speed was 10 cm³/s, and the injection pressure was 2000 bar. The mold provided tensile (ASTM Standard D 638, type IV) and impact (ASTM Standard D 256) specimens. The virgin PTT pellets were also molded as a reference material. The PTT samples are designated PTT-0 to PTT-4, with the number indicating the passes through the extruder before injection molding.

The intrinsic viscosities ($[\eta]$) of PTT were measured in a phenol-tetrachloroethane mixture (50:50 w/w) at 20°C. Weight-average molecular weights (M_w 's) were determined with the Mark-Houwink relationship:²²

$$[\eta] = 8.2 \times 10^{-4} M_w^{0.63}$$

The melt-flow indices (MFIs) of PTT were measured (ASTM Standard D 1238) with a Ceast extrusion plastometer (Torino, Italy) at 250°C and with a 325-g load. Specific volume values were measured in an electronic Mirage SD-120L densitometer (A&D Instruments, Oxford, England) with a resolution of 0.0003 cm³/g with butyl alcohol as the immersion liquid. The infrared analyses were performed in a Nicolet Magna 560 spectrophotometer (Madison, WI) with an attenuated total reflectance objective. The samples were obtained from the molded tensile specimens.

Differential scanning calorimetry (DSC) analyses were performed with a Perkin-Elmer DSC-7 differential scanning calorimeter (Norwalk, CT). The samples were heated from 15 to 270°C at 20°C/min, cooled at the maximum allowed rate, and heated again. Glass-transition and melting temperatures were determined in the second heating scan. Cold-crystallization temperatures were determined in the first heating scan because crystallization did not occur during the second scan. The crystalline contents of the injection-molded specimens were calculated from the crystallization and melting enthalpies of the first heating scan,

with $(\Delta H_m)^o = 145$ J/g for the melting enthalpy of 100% crystalline PTT.^{23,24}

Tensile tests were carried out with an Instron 4301 (Canton, MA) at 23°C and at a crosshead speed of 10 mm/min. The mechanical properties (Young's modulus, yield stress, break stress, and break strain) were determined from the load-elongation curves. Izod impact tests were carried out on notched specimens (notch depth = 2.54 mm, notch radius = 0.25 mm). The notches were machined after molding. At least eight specimens were tested for each determination in both the tensile and impact tests.

RESULTS AND DISCUSSION

The injection-molded PTT specimens were translucent, but after repeated extrusion cycles, they showed a progressive yellowing due to the long exposure to high temperatures and shear stresses in the oxidative environment. Yellowing is an early indication of degradation. Degradation in polymers with processing in the melt state has two main possible results: a change in the chemical structure and a change in the physical structure. The change in the chemical structure is usually seen as a change in both the chemical nature and the molecular weight. The change in the physical structure is usually seen as a change in the crystalline content in crystallizable polymers.

Effects on the chemical structure

A possible change in the chemical structure of PTT was first studied by Fourier transform infrared (FTIR) through a comparison of the absorption bands of the experimental spectra of this work with those previously assigned.²⁵ The FTIR spectra of virgin PTT, PTT-0, and PTT-4 are shown in Figure 1. When the spectrum of virgin PTT is compared with those of PTT-0 and PTT-4, the intensity of the bands of virgin PTT placed at approximately 1465 (CH₂ scissoring mode), 1358 (B_u CH₂ wagging mode), 1043 (A_g C—C stretching mode), and 938 cm⁻¹ (CH₂ rocking mode) is higher, and that of the bands at 1173 and 1018 (A_g CH

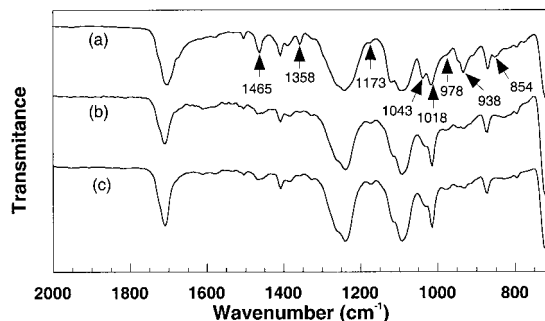


Figure 1 FTIR spectra of (a) virgin PTT, (b) PTT-0, and (c) PTT-4.

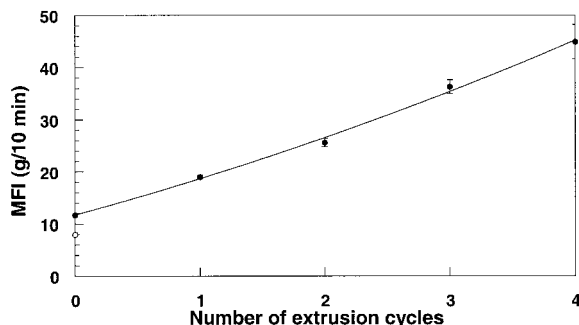


Figure 2 MFI of PTT as a function of the number of extrusion cycles (●). The MFI of virgin PTT is also shown (○).

and B_{2u} CH in-plane bending of phenylene ring) and 978 cm^{-1} (not identified) is lower. Moreover, a small band appears at 854 cm^{-1} (not identified) in virgin PTT, whereas it is not seen in either PTT-0 or PTT-4.

These differences could indicate a change in the chemical structure, but they can also be due to the fact that the crystallinity of virgin PTT is clearly higher than that of processed PTT, as seen later. The FTIR spectrum of PTT is very sensitive to the crystalline content because a change in the crystalline content may lead to a change in the intensity or even to the appearance of new absorption bands.^{25–27} The changes observed in Figure 1 are fairly similar to those reported by Kim et al.²⁵ as a result of changes in the crystalline content. They attributed the new and increased bands in virgin PTT to the crystalline phase; meanwhile, the decreasing bands were assigned to vibrations in the amorphous phase. Therefore, the differences between the FTIR spectrum of the virgin PTT and those of PTT-0 and PTT-4 samples are attributed to their different crystalline contents. The obvious similarity between the spectra of the PTT-0 and PTT-4 samples, which have practically the same crystalline content but suffered reprocessings of clearly different harshnesses, is additional experimental support for the lack of relevant thermooxidative processes with reprocessing. Therefore, the chemical structure of PTT, as in other polymers,^{4,6,7,16,18} particularly aliphatic–aromatic polyesters such as PET¹⁰ and PBT,¹⁴ did not change as a result of the reprocessing.

A recent study on the thermal decomposition of PTT²⁰ indicated a three-step process for its degradation in the presence of air. The first step corresponded to a degradation of PTT chains into smaller fragments by means of an initial end-chain scission. The second stage was attributed to thermooxidative degradation of the small fragments into volatile products, and the third one was attributed to the decomposition of some thermostable structures formed during former degradation processes. If we take into account that no changes in the chemical structure were observed, it appears that only the first stage could be developed under the processing conditions of this work.

TABLE I
[η] and M_w of Virgin and Reprocessed PTT

	[η] (dL/g)	M_w
Virgin PTT	0.92	69,000
PTT-0	0.79	54,000
PTT-1	0.72	47,000
PTT-2	0.69	44,000
PTT-3	0.60	35,000
PTT-4	0.55	31,000

To determine whether chain scission took place as a result of reprocessing, we carried out MFI and [η] measurements, and the results are shown in Figure 2 and Table I. As can be observed, the MFI continuously increased with the number of extrusion cycles, indicating that the molecular weight decreased. This decrease is also proven by the [η] values listed in Table I. The reduction in the molecular weight due to reprocessing was also seen in PET and PBT^{9–14} and other polymers.^{4–7,18}

As can be seen in Table I, a molecular weight reduction occurred with both extrusion and injection molding. However, the main molecular weight reduction was apparently due to the injection molding because the molecular weight reduction from virgin PTT to PTT-0 was higher than that due to any extrusion cycle. Such a difference cannot be seen in the MFI plot of Figure 2, but it must be taken into account that the MFI value is only an indirect indication of the molecular weight. The large molecular weight reduction with injection molding was probably caused by a higher shear level in the injection-molding step.

Effects on the physical structure

The effects of reprocessing on the physical structure of PTT were studied with DSC. As shown in Figure 3, the thermograms were very similar, regardless of the number of reprocessing cycles. The glass-transition (47°C), cold-crystallization, (72°C) and melting temperatures (232°C) remained almost constant with reprocessing. Table II shows the crystalline content of

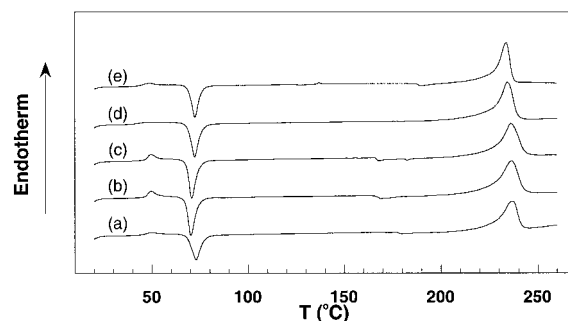


Figure 3 DSC thermograms of reprocessed PTT: (a) PTT-0, (b) PTT-1, (c) PTT-2, (d) PTT-3, and (e) PTT-4.

TABLE II
Crystalline Content (%) of Reprocessed PTT

	Crystallinity (%)
PTT-0	23
PTT-1	23
PTT-2	25
PTT-3	28
PTT-4	27

the reprocessed PTT. The value of the virgin PTT was 48%. It could even be 65%²⁸ because, after molding, the crystallinity increased with time on account of its low glass transition. The low crystalline content of the PTT samples of this study was due to the low mold temperature, which hindered PTT crystallization. The crystalline content increase from PTT-0 to PTT-4 was not very significant because the maximum change (4–5%) and the estimated deviation of the measurement (2–3%) were not very different. However, a possible small crystalline content increase would agree with the molecular weight decrease, which should allow an enhanced mobility of the polymer chains²⁹ and, consequently, make crystallization easier.

Effects on the mechanical properties

The mechanical properties of reprocessed PTT were studied with tensile and impact tests. During notched impact testing, all the specimens broke in a brittle way with very low impact strength values, indicating the notch sensitivity of PTT. The first extrusion cycle led to the most important impact strength decrease (from 32 to 17 J/m). Then, the notched impact strength remained almost unchanged with additional processing cycles.

During tensile testing, whitening of the specimens was observed. This suggests that strain-induced crystallization occurred. For this reason, a DSC analysis was performed after the tensile tests. The obtained crystalline content (roughly 42%) was similar whatever the number of reprocessing cycles and was clearly higher than that before tensile testing (roughly 25%). This indicates that the crystalline content increased as a result of drawing and that strain-induced crystallization took place.

Young's modulus of the reprocessed PTT is shown in Figure 4 against the number of reprocessing cycles. The modulus only slightly decreased with reprocessing. This is because the small decreases after the first and second reprocessing cycles were comparable to the mean standard deviation (± 50 MPa). Modulus changes can be related to a specific volume change of the amorphous phase. For this reason, the density of the various PTT samples was measured, and the specific volume of their amorphous phase was calculated, with the different crystalline contents obtained by

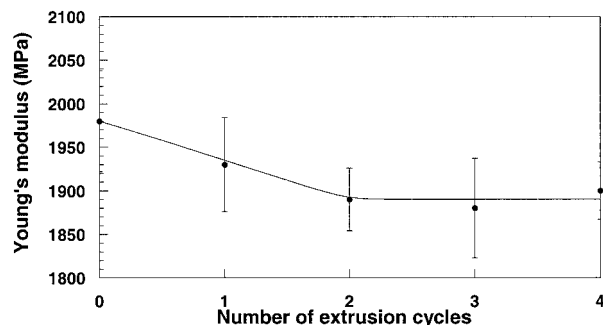


Figure 4 Young's modulus of PTT as a function of the number of extrusion cycles.

DSC taken into account. These crystalline contents were considered representative and unaffected by aging because they remained constant with the time after molding. The specific volumes of the amorphous phase are plotted in Figure 5 against the number of reprocessing cycles. The specific volume of the amorphous phase was calculated with the different crystalline contents taken into account. The specific volume of PTT was the same after the first cycle, but it increased slightly during the second cycle. The change is significant because the estimated standard deviation of the measurement was below 3×10^{-4} cm³/g. Therefore, the change in the specific volume and the probably enhanced molecular mobility of the amorphous phase seem to be responsible for the modulus behavior. The slight changes in the modulus of elasticity were not observed in the yield stress, which remained fairly constant at 45 MPa. These behaviors of the low-strain properties are usually observed in polymer reprocessing.^{6,16,30} With some exceptions,^{2,15} and despite degradation and molecular weight reductions, these properties show slight decreases or even remain constant with reprocessing.

The ultimate properties are shown in Figures 6 (break strain) and 7 (break stress). A decrease in both properties with reprocessing was observed, but even PTT-4 was a very ductile material, with a break strain higher than 200%. The decrease in the break stress is a

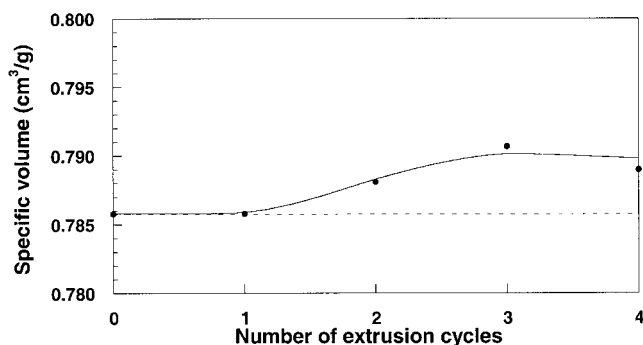


Figure 5 Amorphous specific volume of repeatedly processed PTT.

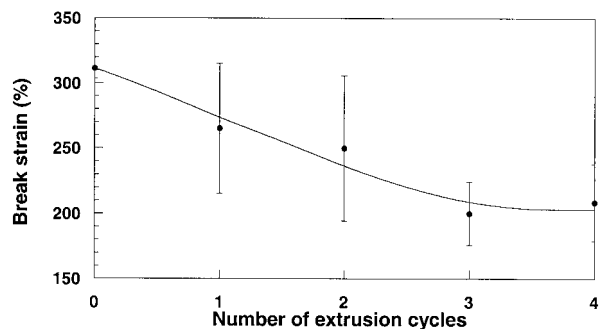


Figure 6 Break strain of PTT as a function of the number of extrusion cycles.

result of that of the break strain because breaking took place in the strain-hardening region of the tensile curves. The decrease in break strain (ductility) could be due to the molecular weight reduction. For this reason, in Figure 8 the break strain values are collected as a function of the molecular weight. As can be seen, a continuous decrease takes place as the molecular weight decreases. This points to the molecular weight reduction as the main structural factor affecting the mechanical properties of the reprocessed PTT.

If we compare this reprocessing behavior with that observed in parent polymers, a sharp decrease in the break strain did not appear in PTT, in contrast with the behaviors observed in PET and PBT reprocessing.^{9,10,12-14} For example,¹⁰ the dramatic ductility decrease observed in PET reprocessing was related to a decrease in the molecular weight below the critical molecular weight. Below this critical molecular weight ($M_w = 8000$), the polymer chains are not long enough to be effectively entangled. This phenomenon has probably not taken place for PTT because the M_w value of PTT-4 of this work (31,000) is expected to be well above the critical M_w . The critical M_w of PTT is unknown, but the chemical structures of PET and PTT are similar.

As can also be seen in Figures 6 and 7, the standard deviation of the ultimate properties in PTT-1 and PTT-2 is clearly higher than that of PTT-0. This is

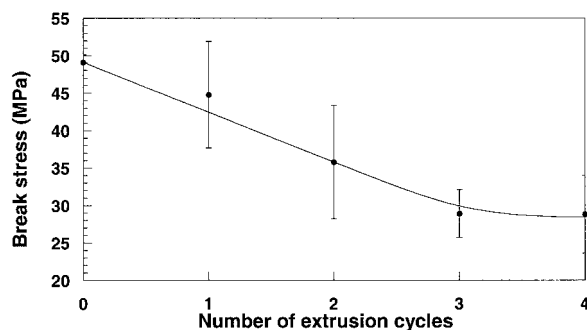


Figure 7 Break stress of PTT as a function of the number of extrusion cycles.

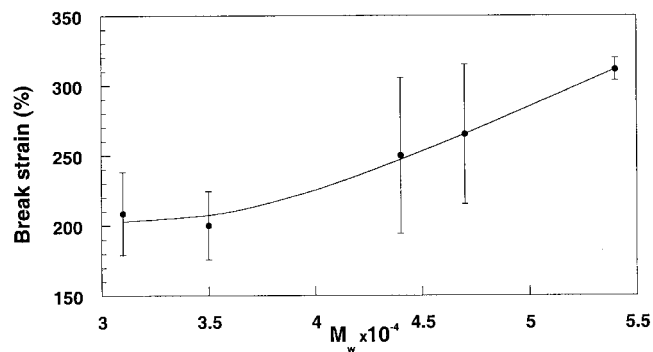


Figure 8 Break strain of PTT as a function of M_w .

because PTT-0 broke during the strain hardening that took place after cold drawing and after a succession of small yielding processes. However, some of the PTT-1 and PTT-2 specimens deformed as those of PTT-0 did, but the rest of the specimens broke during the previous multiple yielding, leading to a noteworthy increase in the standard deviation. All of the PTT-3 and PTT-4 specimens broke during multiple yielding, leading to intermediate standard deviation values. A similar behavior was also observed in PET reprocessing.¹² The formation of a new crystalline structure during orientation due to stretching was suggested as a possible explanation for this behavior.

CONCLUSIONS

Successive extrusion cycles gave rise to a reduction in the molecular weight of PTT, but the chemical structure of the polymer remained unchanged. PTT showed progressive yellowing as a result of reprocessing. A slightly significant crystallinity increase was also seen with reprocessing. The specific volume of the amorphous phase increased slightly, leading to both a slight decrease in Young's modulus and basically constant yield stress values.

The break tensile and impact properties decreased as a result of successive extrusion. However, PTT remained ductile even after four extrusion cycles. This was attributed to a molecular weight above the critical molecular weight for effective entanglements and indicated a favorable reprocessing performance.

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