

Physical–Mechanical Properties and Morphological Study on Nylon-6 Recycling by Injection Molding

MA. JOSEFINA LOZANO-GONZÁLEZ,¹ MA. TERESA RODRIGUEZ-HERNANDEZ,²
EDUARDO A. GONZALEZ-DE LOS SANTOS,¹ JESUS VILLALPANDO-OLMOS¹

¹ Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. No. 140, Saltillo, Coahuila, Mexico

² Fac. de Ciencias Químicas, Universidad Autonoma de Coahuila, Ing Jose Cardenas Valdez y Blvd. V. Carranza, Saltillo, Coahuila, Mexico

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ABSTRACT: The effect of the multiple recycling of nylon-6 by injection molding on its physical–mechanical properties and morphology was studied after each cycle of injection. These studies were made in order to know how many times it is possible to recycle the nylon-6 without significant loss of the physical–mechanical properties. Optical and electronic microscopy were used to evaluate the morphology. Molecular weight changes were determined by gel permeation chromatography (GPC). The nylon-6 was recycled 10 times, until the eighth cycle the properties of the material did not suffer any change. Changes of 10–15% in the properties between nylon-6 with 10 cycles of injection and virgin material were observed. An exception was the percentage of elongation that decreased 70% gradually until in the tenth cycle of injection. The results from GPC show that the molecular weight of nylon-6 increased with recycling ($M_w = 17\%$ and $M_n = 14\%$). With the reprocess was also observed the presence of gels.
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Key words: multiple recycling; nylon-6; injection molding; physical–mechanical properties; nylon-6 morphology

INTRODUCTION

Plastic are common materials in everyday life, which produce big quantities of scrap and that contaminate the environment. Plastic recycling process could eliminate in part this problem, because recycling is the best option to decrease cost and contamination.

The world consumption of thermoplastics is dominated by polyolefines, mainly LDPE (29%),

PVC (18%), PP (16%), HDPE (17%), and PS (8%), in comparison with the 1.5% of consumption of polyamide.¹ It is therefore obvious that polyamide contributes only a little to the plastic waste problem. However, polyamide is one of the most important engineering thermoplastics.

Polymer degradation is an important consideration during processing. Degradation can cause a reduction in physical properties, surface defects, as well as process instability resulting in machine downtime and an increase in quality control costs. They are mechanical, thermal, chemical, and oxidative degradation.²

Nylon-6 plastics are extensively used in the manufacture of automobile parts, engineering products, and textile fibers, because they have

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Correspondence to: Ma. J. Lozano-González (jlozano@polimex.ciqqa.mx).

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many advantages in properties such as high mechanical and impact strength and good processability.³

Nylon-6 with 5% by wt of foreign thermoplastics (PP, ABS, PC + ABS, PBT, POM, PPO/PS) and coatings layers was recycled 5 times by injection molding; the results show that repeated processing on its own causes a slight deterioration in properties and that the impact resistance is particularly affected by the recycling process.⁴

In other studies, different types of regrind nylon-6 and nylon-6,6 with glass fiber were evaluated. The results of the research showed that mechanical and rheological properties decreased with each cycle. In this case, results also showed that generous amounts of regrind can be blended with the virgin resin and still perform according to specification, although 100% nylon regrind should be considered before being used to produce quality parts.⁵

Mechanical properties of products made with recycled materials of two types of polyamide (polyamide 6 and polyamide 12) for injection molding [numerical molecular weight (M_n) = 15000 g/mol and good crystallinity] were studied by Pastuska.⁶ The polyamide-6 and polyamide-12 were injected 7 and 10 times, respectively. The results showed that the materials obtained were getting browner with each cycle of injection, and that the viscosity, density, crystallinity, and water absorption were not influenced by the recycling. It also was suggested that polyamides with an average molecular weight higher than 15,000 g/mol could be influenced by recycling.

The present paper describes the effect of multiple recycling of nylon-6 by injection molding on its physical-mechanical properties and morphology after each cycle of injection. These studies were made in order to know how many times it is possible to recycle of nylon-6 without lost of its physical-mechanical properties in order to obtain a useful material.

EXPERIMENTAL PROCEDURE

Material

Injection molding nylon-6 from Celanese (Mexico) with an melt flow index (MFI) of 19.98 g/10 min and density of 1.1379 g/cm³, average molecular weight (M_w) = 32,000 g/mol, without additives

and without fillers, was used. A Battenfield injection molding machine model BA 750 CDK with conventional screw and plates with standard test cavities were used. The temperature of injection were 210°C to 235°C.

Processing

The nylon-6 virgin (10 kg) was dried in an oven at 80°C by 8 h before injection. Standard specimens for morphology characterization and evaluation of mechanical properties, such as flexural modulus, % of elongation, tensile strength, and Izod impact, were obtained directly from the injection molding machine. After the evaluation, the specimens were granulated in a regrinding mill at pellets size. The granulated material was dried, injected at the same conditions, and the specimens obtained were evaluated again. Thus the nylon-6 was milled, dried, injected, and evaluated until the tenth cycle of injection was obtained.

Characterization and Mechanical Testing

Mechanical properties of nylon-6 virgin and samples of each injection cycle were evaluated using the American Standard Test Method (ASTM) at 23°C: tensile strength, % of elongation (ASTM-D-638; samples dimension 12.7 × 3.4 × 165 mm), and flexural modulus (ASTM-D-790; samples dimension 12.7 × 6.5 mm). These were achieved in an Instron 4801 tensile tester. Impact testing was carried out in an Izod impact tester (Custom Scientific Instrument, CS-137-CB-149 with a mass pendulum of 0.463 kg and 40.64 cm of length) using the ASTM-D-256 (samples dimension 12.7 × 3.17).

Molecular weight was obtained in a Waters Gel Permeation Chromatography equipment model 150-C with 3 columns (2 linear columns and one with size pore of 10⁴ Å). The samples were prepared by dissolving in pure 1,1,1,-3,3,3-hexafluor-2-propanol (HFIP) and diluting with chloroform to reach a final concentration of 1 mg/mL in the chloroform/HFIP mixture (98 : 2 vol %); the mobile phase used was chloroform, and the solvent flow was 1 mL/min at 30°C of temperature. A calibration curve of polystyrene standard (2000 to 2,000,000 Mp) was used.

The gel contents of the samples were determined by means of a Soxhlet extractor. Approximately 0.3 g of the nylon-6 sample was exposed to refluxing *m*-cresol for 12 h.

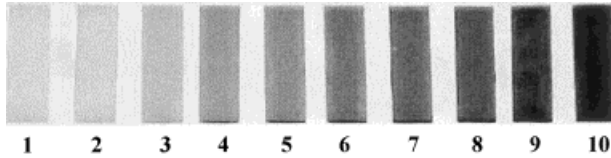


Figure 1 Darkness produced in nylon-6 by each one of the 10 cycles of injection.

Tinius Olsen Plastometer model UE-4-78 and ASTM-D-1238-94 (conditions; 2.16 kg of weight and 230°C of temperature) were used to evaluate the MFI by duplicated.

Optical microscopy was carried out in a Olympus microscope model BX60, with transmitted light and 100× of magnification. Thin films were made by evaporation of formic acid from a nylon-6 solution. The nylon-6 films morphology and from the impact fracture was conducted in a scanning electron microscopy (SEM) TOPCOM model SM-510, with 15 kV for impact fracture samples and 8 kV for films, with an 8 mm working distance. A secondary electrons detector was used to observe the samples.

RESULTS AND DISCUSSION

Processing

In the present work the nylon-6 was reprocessed 10 times in total. Figure 1 show the darkness obtained in the material by each one of the 10 cycles of injection. A huge color change from the virgin material to the material with ten cycles was observed. Levanstokaya et al.⁷ and Marek and Lerch⁸ suggest that the yellowness in the nylon’s results from the formation of pyrrols, which are obtained from the reaction between dicarbonyl and amine group.

Characterization and Mechanical Testing

Tensile strength as a function of number of processes is show in Figure 2; here, a small increment in the tensile strength property of nylon-6 is observed when the number of processes increases. As much as 11% from nylon-6 virgin to the ninth cycle was observed. Due to some processing problem in the cycle number ten, the tensile samples were not tested. Figure 3 shows the changes in elongation (%) obtained with each process. A significant decrease in the elongation (%) was ob-

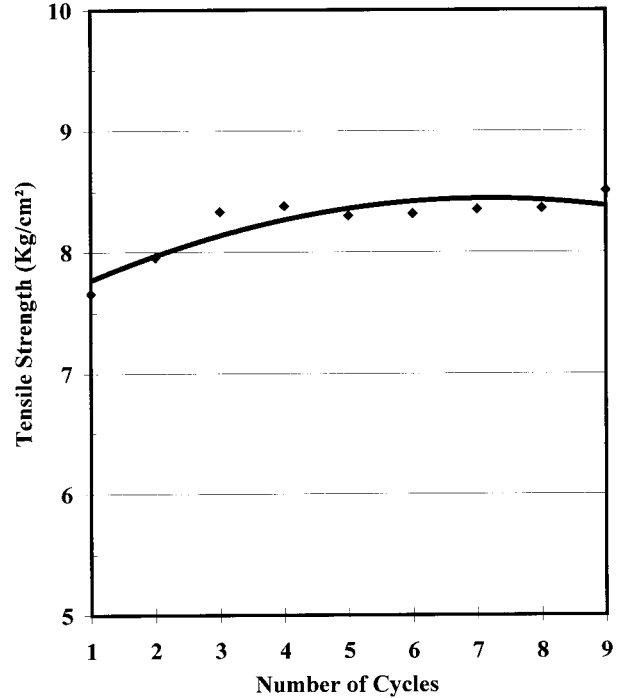


Figure 2 Tensile strength of nylon-6 as a function of number of cycles.

served in the first cycle; then the decrement became less significant—in total. The overall decrement was 70%.

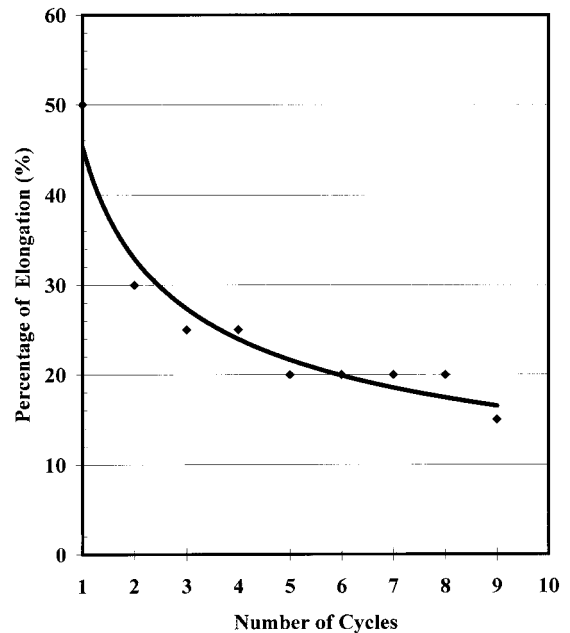


Figure 3 Changes in elongation (%) values obtained with each process.

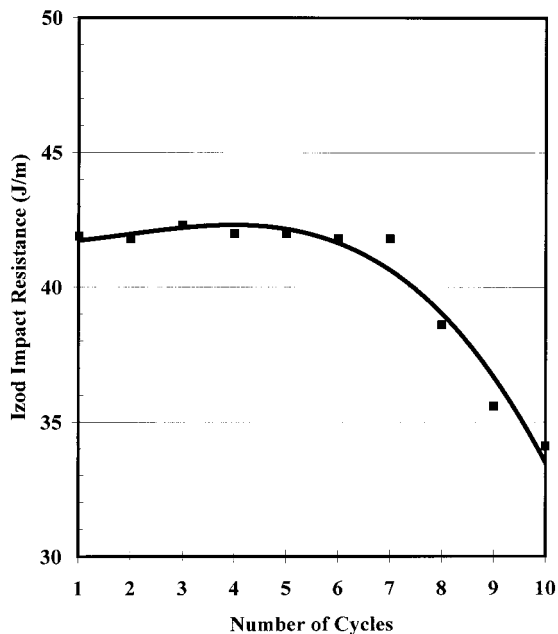


Figure 4 Effect on impact properties of nylon-6 as a function of the number of cycles.

The effect on impact properties of nylon-6 as a function of the number of cycles is shown in Figure 4. The impact resistance had no significant change until the 7th cycle; after this, a decrease in

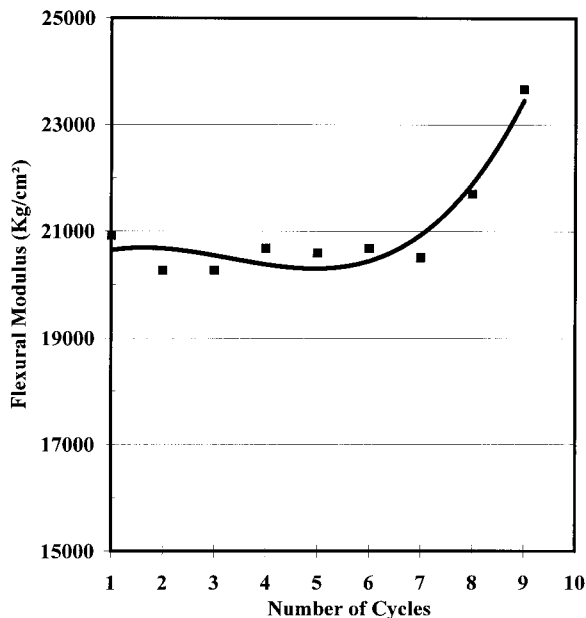


Figure 5 Flexural modulus of nylon-6 as a function of number of cycles.

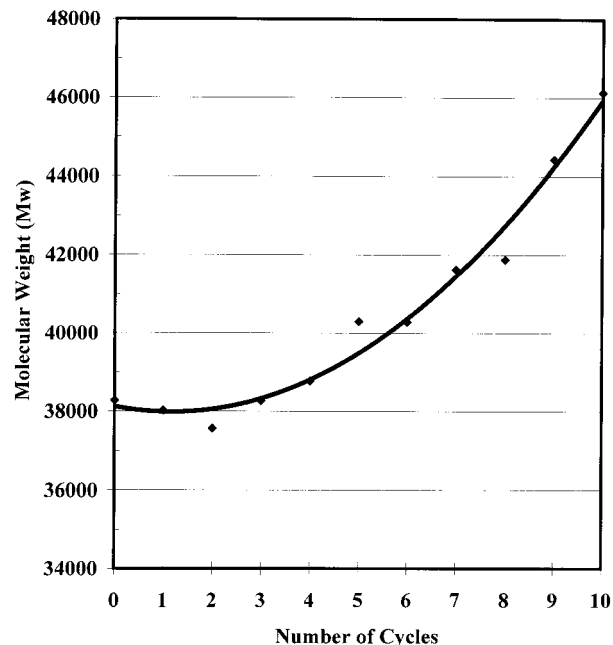


Figure 6 Change in average molecular weight (M_w) of the nylon-6 virgin respect to the reprocessed material.

the impact resistance is observed. Figure 5 shows that the flexural modulus in the recycling nylon-6 is maintained until process number 7; after that, it begins to increase the value significantly. This can be observed also in other properties. The flexural modulus of the nylon-6 with 10 cycles was 10% higher than the nylon-6 virgin. The increase of tensile strength and modulus flexural property during reprocessing can be explained by an increase of molecular weight.^{9,10}

The gel permeation chromatography (GPC) technique was used to obtain the change in average molecular weight (M_w and M_n) of the nylon-6 virgin with respect to the reprocessed material. The results of the M_w and M_n are shown in Figures 6 and 7, respectively. Increases in average molecular weight (M_w) start at its step 5 and rise with the number of injection cycles, as can be seen in Figure 6. On the other hand, Figure 7 show the changes in the average molecular weight (M_n), which is maintained until cycle number 7; after this cycle, the M_n increased significantly until process number 10. The change in the value of M_w was 17% from nylon-6 virgin and process number 10, and 14% for the value of M_n .

The degradation of polymers generally induces main-chain scission and/or crosslinking. In the

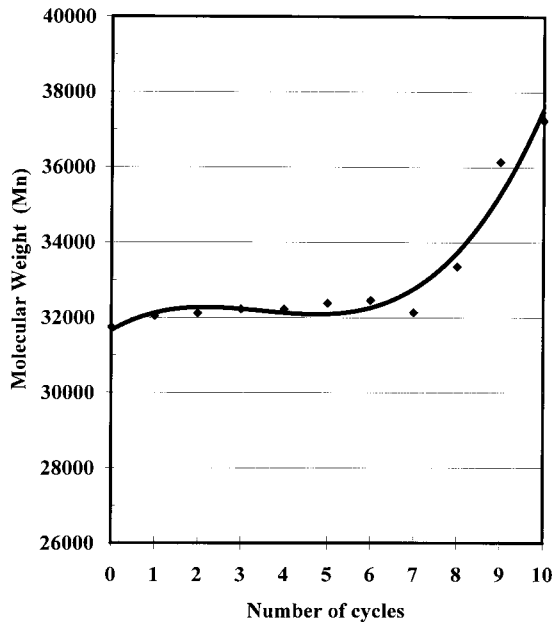


Figure 7 Change in average molecular weight (M_n) of the nylon-6 virgin respect to reprocessed material.

absence of crosslinking, main-chain scissions result in a decrease of both M_n and M_w . If the crosslinked formation is the only process, M_w increases much more rapidly than M_n and has an infinite value at the gel point.¹¹ If the probability of main-chain scission is larger than the probability of crosslinking, M_n and M_w/M_n decrease. Then if the probability of chain scission is smaller than the probability of crosslinking, M_w and M_w/M_n increases, and an insoluble fraction appears. Complete insolubilization of the polymer is only observed if main scission does not occur.¹¹

The results of GPC show that the recombination of broken chains is the dominant effect of degradation, because due the nylon-6 the molecular weight M_w should increase faster than the molecular weight M_n . These results indicate that the broken chains were recombined to form structures of higher molecular weight and gels.

Figure 8 shows the change in the MFI. In this figure it can be observed that the MFI decreases with the number of injection cycles. As is known, the chains of material with high molecular weight are tangled more easily than the chains of material with low molecular weight, and therefore the flow resistance goes high. If the MFI decreases, the viscosity of the material is high (degradation by increase the molecular weight and by crosslinking); and if the MFI increases it indi-

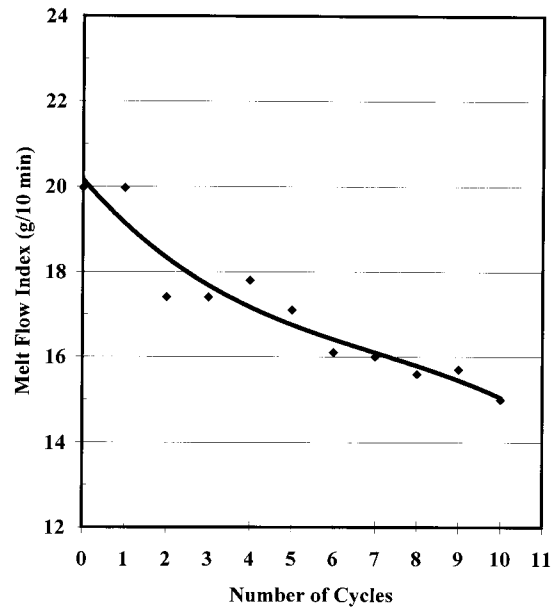


Figure 8 Decrement of the nylon-6 MFI with the increment in the number of cycles.

cates less viscosity of the polymer (degradation by broken chain).¹²

Figure 9 shows the gel content as a function of number of processes. It can be observed that increasing the number of molding operations up to

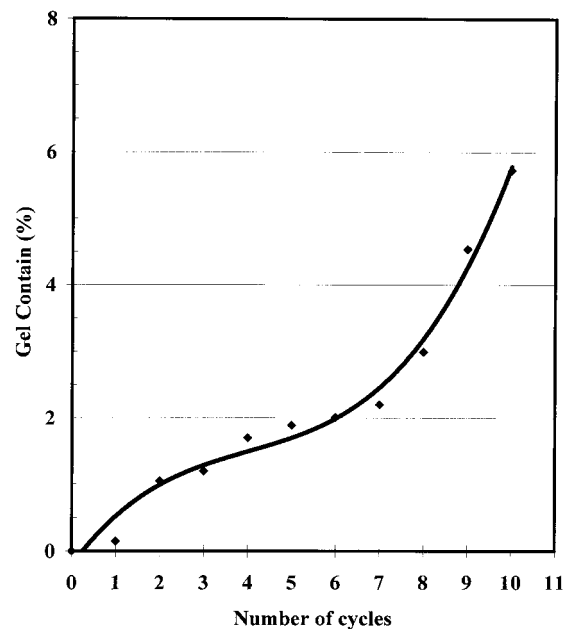


Figure 9 Gels content results obtained in nylon-6 by each of the tenth processes.

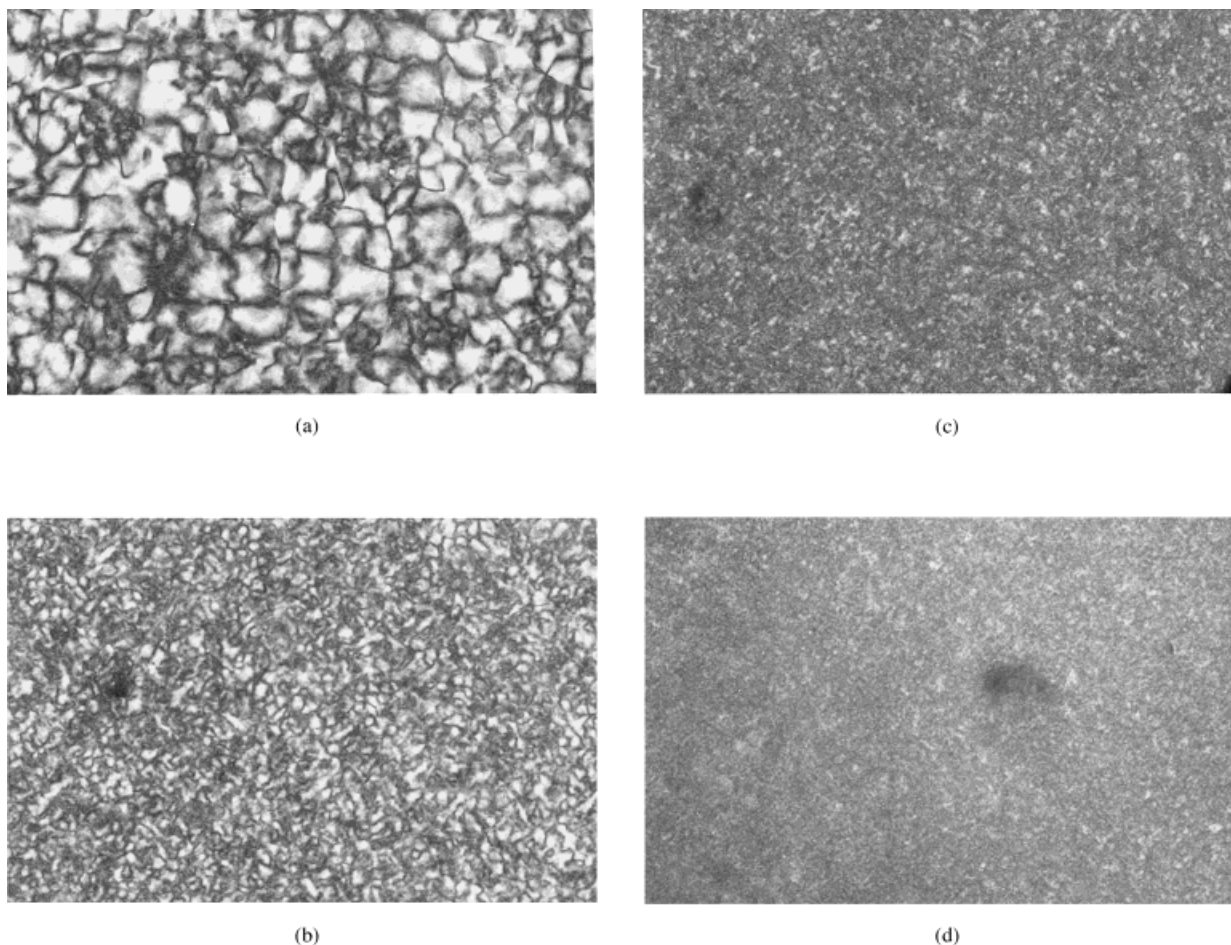


Figure 10 Microphotographs of spherulites obtained by optical microscopy at $600\times$ magnifications: (a) nylon-6 virgin, (b) first cycle, (c) fifth cycle, and (d) tenth cycle.

two times results in an increment in the gel content (%). The increase of gel content confirms that the multiple recycling of nylon-6 induces recombination of broken chains.

Optical polarized light photographs and SEM photographs for nylon-6 virgin and after each cycle of injection were used to observe the qualitative change of the spherulite size. Optical polarized light photographs obtained at 600 magnification, a decrement in the spherulite size for nylon-6, is shown in Figure 10(a–d). It also can be seen that the spherulite size decrement starts as early as the first cycle of injection.

SEM was used to obtain the microphotographs at 5000 magnification; the size of spherulite was observed using an image analyzer (Table I). Also as seen by optical microscopy, the spherulite size is reduced when the nylon-6 is injected into more

cycles [Fig. 11(a–d)]. This may be due to unmelted particles that are formed from polymer degradation and act like nucleation agents, which form small crystals and therefore increase the crystallization temperature.¹³ Hence as the number of injection cycles increase, the spherulite size becomes smaller and shows imperfections in the crystalline regions.

Table I Size Spherulite of Each Cycle

Number of Cycles	Size Spherulite (μ)
0 ^a	4.22
1	3.42
5	0.76
10	0.63

^a Pellets of virgin material before the first process.

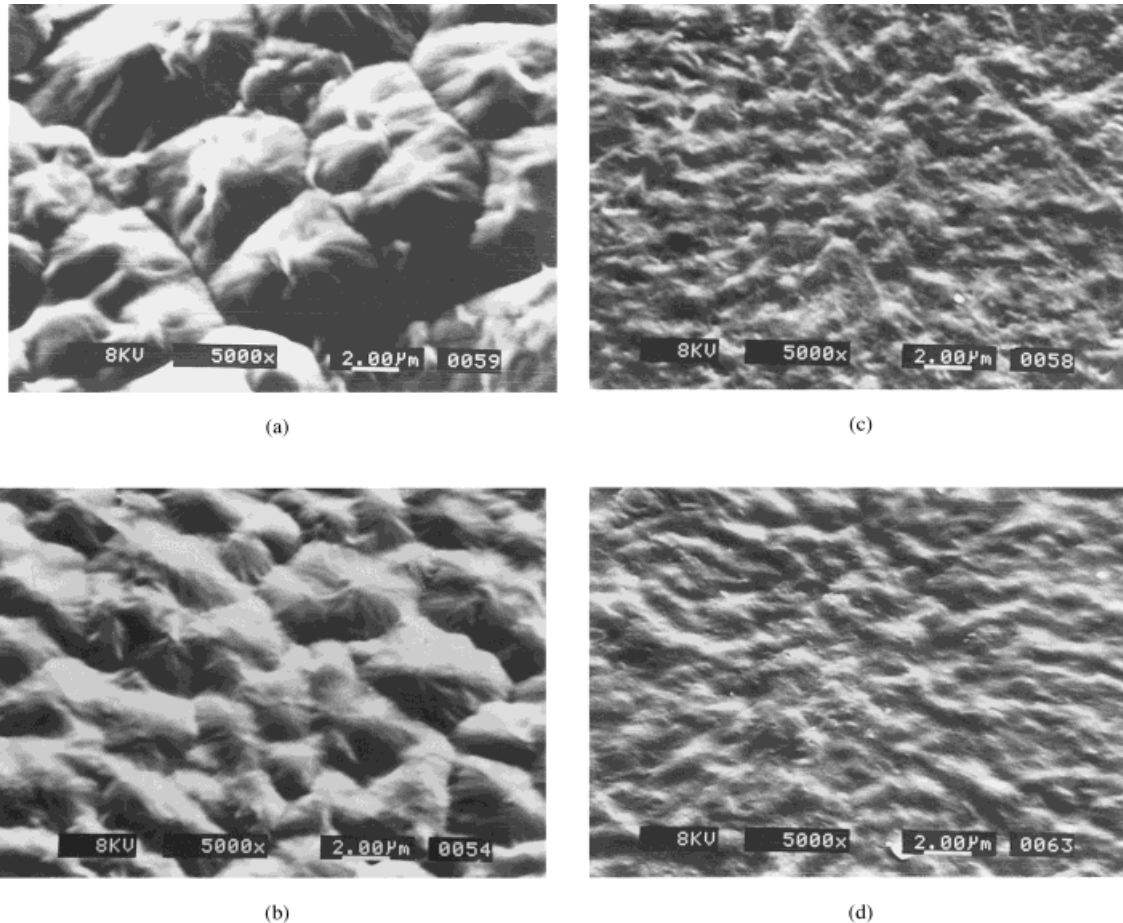
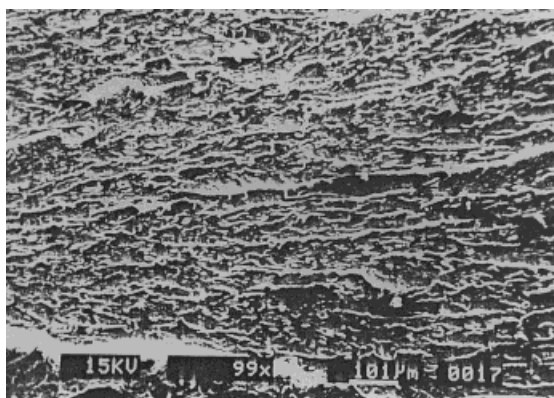


Figure 11 Microphotographs of spherulites obtained by SEM at 5000 \times magnifications: (a) nylon-6 virgin, (b) first cycle, (c) fifth cycle, and (d) tenth cycle.

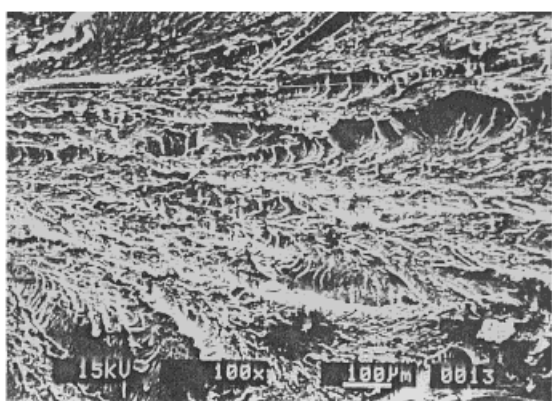
Impact test fracture analysis for the nylon-6 (first, fifth, and tenth cycle) was carried out by SEM for determination of the mode or cause of failure, and to correlate the mechanical data. Microphotographs with 100 \times magnification were obtained and are shown in Figure 12. In microphotograph (a) it can be observed that the fracture morphology of the nylon-6 has a brittle fracture morphology since the first cycle a classical form of the nylon-6. However, in microphotographs (b) and (c) the nylon-6 samples with the fifth and tenth cycle are observed as fracture ridges and with less adherence. This is due to gel particles and contamination particles that produce these defective sites. The latter is in agreement with the decrease in the impact resistance for the last three or four cycles; therefore when the number of cycles increased, the brittleness of the nylon-6 increased.

CONCLUSIONS

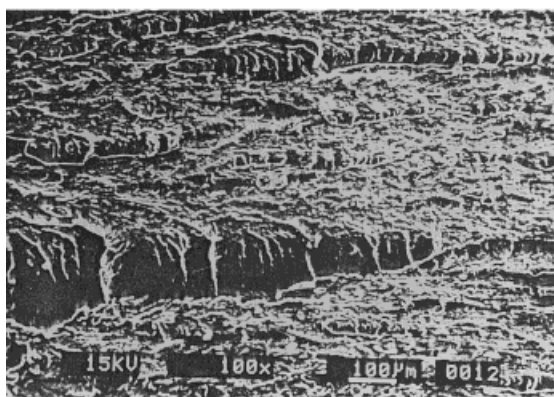
It is obvious that the cause of the decrement in the physical-mechanical properties of nylon-6 was polymer degradation. Nylon-6 was recycled up to 10 times. Until the eighth cycle the material properties were almost constant. Changes of 10–15% in the properties between nylon-6 with 10 cycles of injection and nylon-6 virgin were observed. An exception was the percentage of elongation, which decreased about 70% between the first and tenth cycle of injection. This property showed to be very sensible to degradation of nylon-6. The results from GPC show that the molecular weight increases with the recycling ($M_w = 17\%$ and $M_n = 14\%$)—hence recombination of broken chains is the dominant effect, rather than chains scission and low molecular weight segments. An increment of gel content with the reprocess was also observed.



(a)



(b)



(c)

Figure 12 Microphotographs of the impact test fracture by SEM at 100 \times magnifications: (a) first cycle of nylon-6, (b) fifth cycle, and (c) tenth cycle.

The morphology of nylon-6 was considerably affected with the reprocessing; the spherulite size decreased as the number of injection cycles increase. The MFI decreased as the number of cycles increased; this indicates that the type of degradation in nylon-6 is by recombination mechanism.

Nylon-6 can be processed up to seven times without further effect on its physical-mechanical properties and morphology; the only change registered was the color, as early studies report.⁶ However, this problem cannot be significant if pigmented items are produced. Beyond the seventh cycle, pieces of less quality are obtained; however, by mixing with the virgin material an improvement in the properties may be achieved. Under the present condition of this work, exceeding 10 cycles is not recommended, as significant decrement in properties and injection problems were observed.

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