Structure and Physical Properties of Reprocessed Poly(ether imide)

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ABSTRACT: The effects of reprocessing by injection molding on the structure and properties of poly(ether imide)(PEI) were studied. The chemical structure of PEI does not change after reprocessing. However, the weight-average molecular weight decreases after the first and the second injection cycles, after which it stays constant. Despite the harsh conditions used, the thermal resistence and the small strain mechanical properties were unaffected by the application of successive injection molding processes to the 100% regrind PEI specimens. The tensile ductility and energy at break showed a decrease parallel to that of the molecular weight. However, the Izod impact strength was constant, probably due to the differences in strain rate and mode of deformation between the tensile and impact tests. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1601–1607, 1997

Key words: poly(ether imide); reprocessing; degradation; molecular weight; mechanical properties; thermal properties

INTRODUCTION

A great deal of attention has been devoted in recent years to the recycling of plastics.[1–3] The interest in recycling is mainly ecological in commodity, high-volume consumption plastics, but may be economic in high performance expensive polymers. The recycling of scrap from processing operations, like injection molding, is widely carried out in the plastics industry. It is called primary recycling or reprocessing and involves grinding the scrap and mixing it with the virgin material before processing. The successive temperature–shear stress and strain cycles inherent in reprocessing may lead to thermal, thermooxidative, or mechanical degradation that can produce chain scission, grafting/crosslinking, or unsaturation–cyclization due to side chain reactions,[4] and to a loss of properties.[5]

The knowledge of the degradation origins and the effects of these processes on the structure and properties of plastics materials is essential if reprocessing is to be carried out. This is because the former indicates which are the most suitable additives to control degradation and because the latter provides basic information about the maximum amount of recycled polymer that may be mixed with the virgin one while maintaining a minimum level of mechanical properties.

Poly(ether imide)(PEI) is a high performance amorphous thermoplastic based upon regular repeating ether and imide linkages. The aromatic rings give stiffness to the polymer, while the ether linkages allow for good melt-flow characteristics and easy processing. PEI has a glass transition temperature (T_g) of approximately 220°C and is the newest generic engineering polymer widely introduced into the market.[6] Nowadays it is only

commercialized by General Electric Plastics under the trade name ULTEM, in both the unmodified and reinforced forms. Its good level of properties makes PEI suitable for a clearly increasing number of applications that require, among other properties, high temperature stability, high physical strength, and easy processability in conventional equipment. Because of the relatively high price of PEI, reprocessing appears to be advantageous or even necessary. However, no work has been carried out, to our knowledge, on the effects of reprocessing on the structure and properties of PEI.

For these reasons, in the present work a systematic study was carried out on the effects that successive injection molding cycles have on the chemical structure, molecular weight, and mechanical and thermal properties of PEI. A low processing temperature, which additionally indicates the possibility of blending with other polymers, was used and only reprocessed PEI was employed instead of mixing it with virgin material. Both parameters were chosen with the aim of enlarging the degradation effects and, thus, making them easier to discern.

EXPERIMENTAL

PEI (Ultem 1000, General Electric Plastics) was supplied by Polymerland Guzman, S. A. (Valencia, Spain). PEI has the following chemical structure:
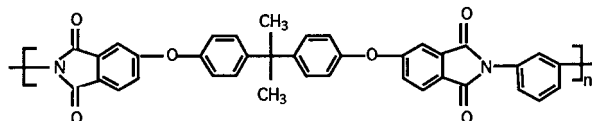
It has an intrinsic viscosity $[\eta] = 0.494$ dL/g, as determined in chloroform at 23°C. It was dried at 135°C for 12 h in an air oven before each processing cycle to avoid possible degradation caused by moisture.

The successive injection molding cycles were carried out in a Battenfeld BA230E reciprocating screw injection molding machine at a barrel temperature of 330°C and a mold temperature of 80°C. The injection speed was 23 cm^3/s and the screw rate during plasticization was 110 rpm. The injection pressure was 2900 bar. The mold provided tensile (ASTM D638, type IV) and impact (ASTM D256) specimens. After each molding cycle, 12 tensile and impact specimens were selected. The rest of the material was pelletized and processed again.

Intrinsic viscosities of PEI after each processing cycle were measured at 23°C in chloroform. Molecular weight measurements were carried out in a Waters ALC-GPC 150 chromatograph, using chloroform as the solvent and at a temperature of 30°C. The melt flow index (MFI) was determined using a Ceast 6540/011 melt flow indexer. A melt temperature of 315°C and a load of 5000 g were used. Possible changes in the chemical structure of PEI after each processing cycle were checked by FTIR using a Nicolet 5DXC spectrophotometer. Samples for FTIR were prepared in the form of thin films by casting from solutions of the polymer in chloroform.

Calorimetric analysis was carried out in a Perkin–Elmer DSC-7 calorimeter. The glass transition temperatures (T_g) were determined in the second scan carried out from 50 to 280°C at 20°C/min. Cooling between both scans was carried out at the maximum speed available for the calorimeter. Vicat softening temperatures were measured using an ATS-FAAR MP/3 HDT-Vicat tester according to ASTM D1525 (50°C/h and 1000-g load).

Tensile tests were carried out using an Instron 4301 at 23°C and at a crosshead speed of 10 mm/min. The mechanical properties (Young's modulus, E; yield stress, σ_y; break stress, σ_b; and elongation at break, ε_b) 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. A minimum of eight specimens were tested for each determination in the tensile and impact tests.

RESULTS AND DISCUSSION

Structural Effects

During reprocessing, the original amber coloration of PEI darkened progressively. This is a first indication of degradation; however, transparency was maintained.

The most usual main degradation effects in melt-reprocessed polymers are either a change in the molecular weight, a change in the chemical nature, or both effects.[5] The first possibility was tested by intrinsic viscosity, GPC, and MFI, and the second by FTIR. Figure 1 shows the FTIR spectra obtained for unprocessed and PEI processed 5 times. As observed, no appreciable difference exists between the spectra, with the excep-
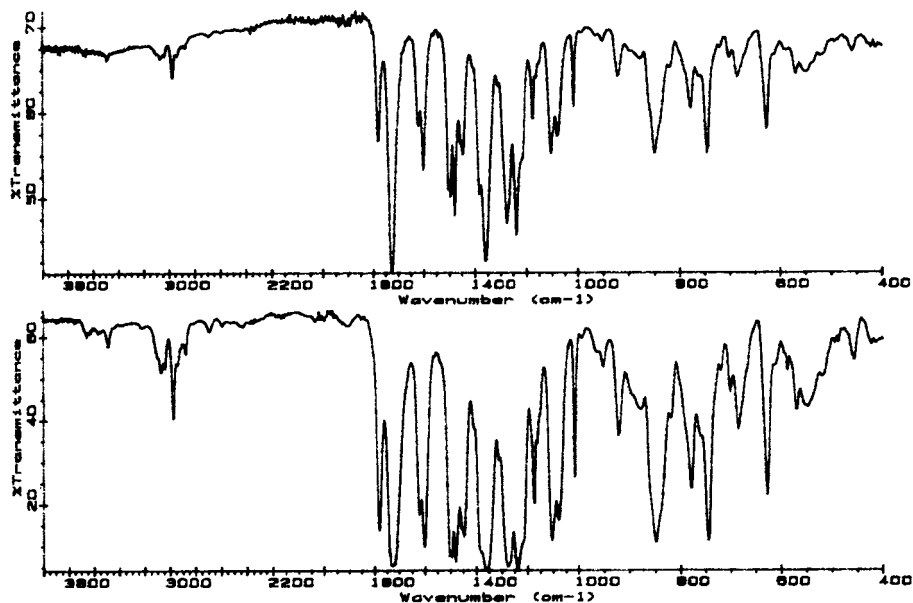
Figure 1   FTIR spectra of unprocessed (top) and five times processed (bottom) PEI.

tion of the intensity of the spectra, which was determined by the thickness of the films. So, the chemical structure of PEI does not change significantly as a consequence of reprocessing in the conditions of this work.

With respect to molecular weight, the intrinsic viscosity and the MFI are parameters indicative of possible changes. For this reason, they are represented in Figure 2 against the number of processing cycles. As can be seen, the variation observed in the MFI is fully consistent with that of the intrinsic viscosity plot. Both plots indicate that the molecular weight of PEI decreases during

the first and second cycles, but that it remains constant thereafter. Molecular weight values are not easy to obtain from either MFI or viscosity values, but a semiquantitative estimation of the molecular weight decrease may be made from GPC chromatograms. Because the Mark–Houwink constants of PEI were unknown, the molecular weights were estimated using the constants for polystyrene (PS) in the same solvent.

The results obtained by GPC are summarized in Table I. As can be seen, the number-average molecular weight (M_n) and the polydispersity (M_w/M_n) do not follow any clear tendency. Thus,
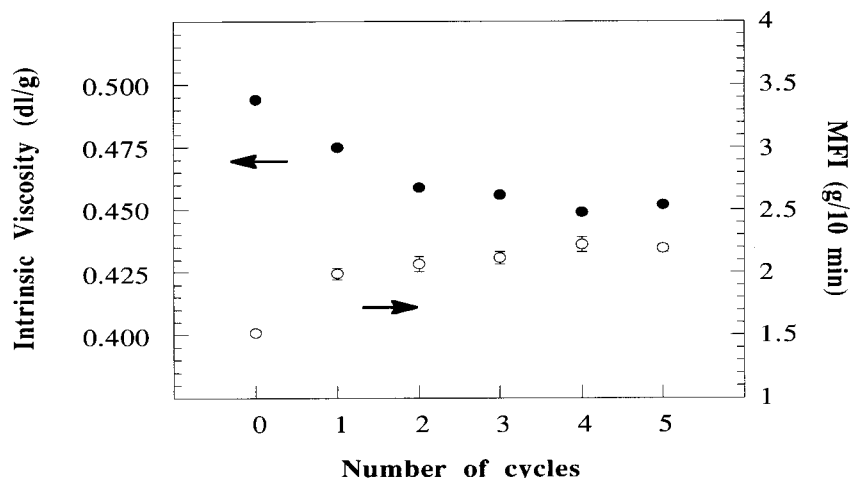

Figure 2   (●) Intrinsic viscosity and (○) MFI of PEI as a function of the number of injection molding cycles.

Table I Molecular Weights, as Polystyrene, Obtained by GPC for PEI after Successive Injection Molding Cycles

No. Processing Cycles	M_w	M_n	M_w/M_n
0	46,200	8600	5.37
1	40,900	7500	5.47
2	38,900	8300	4.69
3	39,100	7500	5.18
4	39,500	8200	4.83
5	38,700	7500	5.17

these two parameters may be considered practically constant within the experimental error. However, the weight-average molecular weight (M_w) decreases after the first and second processing cycles, then remaining constant up to the fifth processing cycle. This behavior of the M_w by GPC closely corresponds with that of the viscosity and that of the MFI. Its difference with the behavior seen in M_n is consistent with the more direct relation between M_w and melt viscosity.[7] The larger decrease in M_w compared with that in M_n indicates that degradation principally affects the higher molecular weight polymer.

The variation of molecular weight with reprocessing of PEI displayed by means of the MFI, viscosity, and GPC data, was somewhat unexpected. This is because usually[8–10] a more monotonous decrease in molecular weight (increase in MFI) is observed. The constancy of the molecular weight after the second and subsequent processing cycles may be explained by taking into account that when mechanical degradation arises, an exponential decrease in molecular weight versus shearing time exists[11] until an apparent limiting molecular weight, $M_{\lim}$ is reached. $M_{\lim}$ depends on the nature of the polymer and on the processing conditions. Here it appeared to be very high, $M_w \sim 39,000$, and this value was almost reached, under these shear stress conditions, after the second injection molding cycle. This $M_{\lim}$ is higher than the minimum molecular weight for the entanglements to be effective, also called the critical molecular weight. This is because, as is known and found in the case of poly(ethylene terephthalate) (PET)[12] the material becomes very brittle below the critical molecular weight while the mechanical properties, ductility for instance, are maintained at a reasonable level in PEI at the $M_{\lim}$.

With respect to the origin of the observed molecular weight decrease during reprocessing, the most usual effects are mechanical or chemical. Oxidative degradation or hydrolytic degradation through the imide groups[4] should give rise to new chemical structures that were not observed in the FTIR spectra, so they must be discarded as the principal source. Additionally, it has been shown[13] that thermal degradation of PEI at high temperatures would be initiated at the isopropylidene moiety of the bisphenol-A units and would be followed by chain scission or crosslinking. Crosslinking may be demonstrated by the appearance of an insoluble fraction of the polymer and by the increase in molecular weight before the insoluble fraction appears. In our case, none of these effects was observed, so crosslinking had to also be discarded.

With respect to a mechanical origin of degradation, the observed molecular weight variations indicated that chain scission took place; so that it was the main degradation mechanism in this case. Chain scission should be caused by the shear stresses and strains during processing to the detriment of thermal degradation. This is because they are more likely[14] than high temperature to give rise to chain scission and because of the relatively low reprocessing temperature selected.

This fairly good response after reprocessing agrees with the reported high resistance of PEI to thermal, oxidative, and mechanical degradation[15] that is due to the high stability of the ether and imide linkages. Thus, mechanical degradation of the longest PEI molecules due to shearing in the plasticization unit of the injection molding machine appeared to be the main cause for degradation in the present case.

Physical Properties

Previous to the mechanical properties, some thermal properties were also determined. One of the most interesting features of PEI is its remarkable thermal resistence due to its high T_g. Because molecular weight variations may lead to T_g changes,[16] the T_g values and the Vicat softening points of PEI subjected to successive injection molding cycles were determined. They were approximately 216 and 207°C, respectively, and were irrespective of the number of injection molding cycles. This indicates the lack of effect of reprocessing on the thermal resistence of the polymer.

Different behaviors are observed in the mechanical properties of thermoplastics when the effect of reprocessing is considered. They are difficult to compare because the equivalent processing
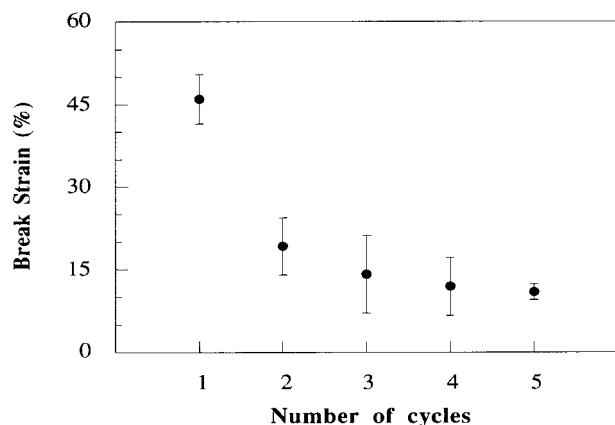
Figure 3 Ductility of PEI against the number of injection molding cycles.

conditions (temperature, for example) in different polymers are not evident. However, it appears[5,9,14] that constancy of small strain properties after reprocessing is a usual response. This response, although with exceptions,[17] is not usually maintained in fracture properties.[5,12,14] In the present case, the Young's modulus and the yield stress, which was also the tensile strength, also remained approximately constant, as is usual, with mean values of 3300 and 106 MPa, respectively.

The ductility of PEI is represented against the number of injection molding cycles in Figure 3. As can be observed, it decreased after the first and second processing cycles and remained practically constant thereafter. The ductility after five injection cycles decreased to approximately 33% of the original value after a single molding cycle. However, it remained in any case higher than the yield strain (approximately 5.4%) and the specimens developed full necking even after five processing cycles. Both the natural draw ratio and the height of the yield peak, measured by the difference between the yield and the drawing stresses, remained constant despite the molecular weight and ductility decreases.

The variation of ductility of PEI with reprocessing shows a remarkable parallel behavior with the variation of M_w, MFI, and intrinsic viscosity shown in Table I and Figure 1. Thus, given that the M_w decrease appears as the only main degradation process, a relation between ductility and molecular weight does seem to exist. Decreases in ductility were also seen and were related to the molecular weight in the reprocessing of other thermoplastic polymers.[8,9,12,16] These ductility decreases may be a consequence of other factors

when more complex materials, blends for example, are considered.[10,18,19]

The number of cycles–ductility plot, and that seen before of the molecular weight also against number of cycles, allow us to relate the extent of the degradation mechanism with its effect on ductility. Among the three possible parameters, that is, MFI, intrinsic viscosity, or M_w related to PS, which might represent the degradation extent, MFI was chosen, due to its more controlled accuracy. It is shown in Figure 4 against ductility and provides useful information concerning the use of reprocessed PEI.

The break stress of PEI showed a behavior qualitatively similar to that of ductility. However, the variation of the break stress from the first to the fifth cycle was only 8%. This is due to the fact that breaking of the tensile specimens took place in all cases in the flat cold-drawing region of the tensile curves, and consequently the break stress was practically unaffected by the decrease in ductility seen in Figure 3. Finally, the variation with reprocessing of the energy absorbed by PEI in the tensile test showed a behavior very similar to that of ductility. This was because looking at the two parameters that mainly draw the area under the stress–strain curve, that is, the yield stress and the elongation at break, the former remained constant with reprocessing and the latter changed in the same way as ductility.

The energy at break of PEI was also measured by means of the Izod impact test and is shown against the number of processing cycles in Figure 5. As observed, the behavior of the impact strength with respect to the number of injection cycles is different from that of the ductility, and as a consequence, from that of the energy at break
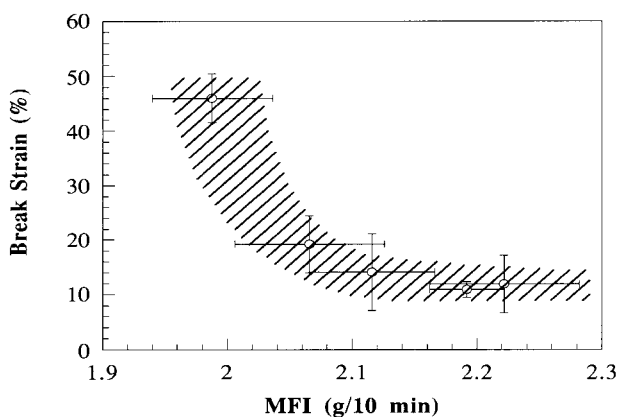

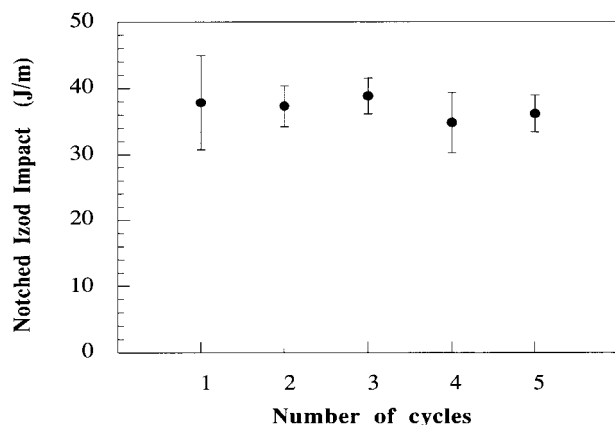**Figure 4** Ductility as a function of MFI for reprocessed PEI.

Figure 5   Notched Izod impact strength of PEI as a function of the number of injection molding cycles.

obtained from the tensile tests. This is because it remained practically constant with the number of molding cycles. This different behavior may be influenced by the inherent differences between tensile and impact tests, which include strain rate, stress distribution, and mode of deformation, among others. But the probable most important reason is that in the impact test of PEI, the energy required to initiate the crack was very high compared to that necessary to propagate it (unnotched and notched Izod impact strength equal to 1300 and 53 J/m, respectively).[20] In tensile tests both contributions to toughness are taken into account, but almost only the latter in the case of notched impact tests. Thus, the differences between the ductility and impact strength plots indicate that reprocessing does not affect the propagation energy, but mainly affects the energy to initiate fracture. Although sometimes it does not take place, for example in ABS[10] or PEEK,[17] the fact that ductility decreases are larger than those of the impact strength also takes place in reprocessed PC,[8] PC/PSU,[19] HDPE,[21] HIPS,[18] and PC/ABS.[10] This indicates that ductility is usually more sensitive to reprocessing than impact strength.

The above-mentioned results concerning reprocessing by injection molding of PEI indicate that, in spite of the molecular weight decrease during the initial cycles, and the consequent deterioration of several mechanical properties, these mechanical properties were maintained at a relatively good level even after five processing cycles. This stability in the properties includes: the constant Young's modulus, yield stress or tensile strength, and notched impact resistence; the very slight decrease in break stress; and although the

elongation at break decreases clearly, the ductile behavior of all the reprocessed materials.

CONCLUSIONS

Reprocessing by injection molding of PEI gives rise to a decrease in the M_w of the polymer during the first and second processing cycles. After the third and subsequent cycles, the M_w reaches an approximately constant value. This behavior is indicated by intrinsic viscosity, MFI, and GPC measurements. The number-average molecular weight and the polydispersity appeared independent of the number of processing cycles. The chemical structure of the polymer is not affected by reprocessing. Degradation appears to be mainly mechanical.

The thermal resistance of PEI remains unchanged, while the mechanical properties are affected to a different extent by reprocessing. Modulus and yield stress remain constant with reprocessing, following the usual behavior. The break properties more clearly show the effect of reprocessing and of the concomitant molecular weight change. Thus, the ductility decreases in the first two cycles and its relation to the number of cycles is parallel to that of the intrinsic viscosity. However, PEI always yields, even after five cycles. The decrease in the energy at break measured from the tensile test is not reproduced by the impact test, probably due to the inherent differences between both testing methods. Thus, the properties of PEI are maintained at a good overall level, even after the 100% regrind and low temperature reprocessing experimental conditions of this work.

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