

Structure and Properties of a Poly(amino ether) Resin After Reprocessing in the Melt State

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ABSTRACT: The effects of reprocessing by extrusion for up to five cycles, at both the usual (200°C) and an extreme (230°C) temperature, on the structure and mechanical properties of a poly(amino ether) (PAE) resin were studied. A slight darkening and viscosity increase was observed, mainly upon reprocessing at 230°C. The melt flow index and solubility analysis indicated that grafting and crosslinking reactions took place, respectively, after reprocessing at 200 and 230°C. The Young's modulus and the yield stress of PAE increased slightly with successive extrusion cycles. This was attributed to the viscosity-induced increase in orienta-

tion, and to a minor extent to the partially grafted/crosslinked nature of the samples. The decrease in the ductility was more noticeable in the samples reprocessed at 230°C, and was attributed to the reduced ability to elongate of partially grafted and partially crosslinked structures present after reprocessing, respectively, at 200 and 230°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1368–1373, 2006

Key words: degradation; reprocessing; mechanical properties

INTRODUCTION

In recent decades, the interest in recycling polymeric materials by means of thermomechanical techniques (the so-called physical recycling or reprocessing)^{1,2} has increased. The reuse of polymeric materials is important for both environmental as well as economic reasons. For example, in the manufacture of injection molded parts with thermoplastic polymers, significant amounts of material are usually wasted on scrap material from sprues and runners, as well as faulty parts. Depending on the process, this may constitute a significant percentage of the plasticized material whose reuse is today a need from an economic point of view. The environmental reason arises mainly from the wide spread of applications of plastics and the continuous increase in consumption that leads to serious waste disposal problems, mainly in industrialized countries. Waste products arising from packaging applications, which is the main plastics consumption sector, have contributed greatly to the perception of plastics as a major environmental problem.^{1,3,4}

As a consequence of the repeated processing cycles and the high temperatures and intensive shearing de-

veloped during processing, the possibility of thermal and/or mechanical degradation must be taken into account. Degradation may appear in the form of either physical changes in the structure, or chemical changes by reactions leading to chain scission, grafting, or crosslinking.² As both changes may deteriorate the polymer properties, it is of great importance to know how and to what extent reprocessing affects structure and properties, and how many processing cycles a material can bear, while maintaining an acceptable performance. This information is necessary to decide the amount of reprocessed material, which can be added to virgin material without a significant reduction in a given property.

Studies on the nature of degradation caused by reprocessing and on the effects of degradation on the properties of polymers have been conducted for a large number of thermoplastics.^{5,6} Among others, commodity plastics such as polyethylene^{4,7,8} and polypropylene^{1,3,9}; engineering polymers such as bisphenol A polycarbonate (PC),^{10–12} poly(ethylene terephthalate) (PET),^{13,14} poly(trimethylene terephthalate) (PTT),² poly(butylene terephthalate) (PBT),¹⁵ and polyamide 6 (PA6)^{16,17}; high performance polymers such as poly(ether imide) (PEI)¹⁸ and poly(ether ether ketone) (PEEK)¹⁹; as well as liquid-crystal polymers²⁰ and polymer blends^{21–24} have been studied.

Poly(amino ether) (PAE) resins are a new family of thermoplastics, characterized by very good barrier properties, excellent adhesion to different substrates, high optical quality, low color, and good mechanical

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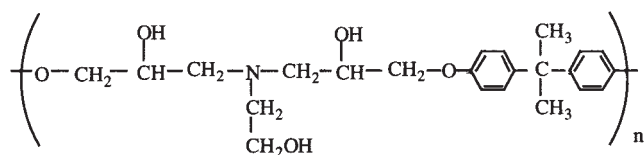
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toughness.²⁵ Their main applications are in the packaging industry. A resin obtained by polycondensation of the diglycidyl ether of bisphenol-A and ethanolamine (PAE) is one of the best known PAEs. Because of its recent development, this resin has been reported only in a few papers^{25,26} that analyze the synthesis and thermal, mechanical, and barrier properties as well as the effects of structure on properties. Studies on PAE blends with PA6,²⁷⁻²⁹ an amorphous polyamide,³⁰ PBT,³¹ and with PET modified with PBT³² have been recently carried out in our laboratory. Another PAE has been used as a compatibilizer for PA6/PBT blends.³³ However, despite the interest in PAE, to our knowledge no literature report has dealt with either its reprocessing or degradation. Blending PAE with other thermoplastics before either blow or injection molding supposes an additional processing.

In this work, we analyze the effects of reprocessing by repeated extrusion cycles on the structure and properties of PAE. The polymer was always finally injection-molded to obtain testing specimens. The effect of the processing temperature was investigated by using both a typical temperature for PAE (200°C) and an extreme value (230°C). The possible changes in the chemical structure and the molecular weight were tested by Fourier Transform infrared spectroscopy (FTIR) and melt flow index (MFI) measurements, respectively. Dynamic-mechanical analysis (DMA) was used to assess the effects on the physical structure. The effects of structural changes of PAE on the mechanical properties were determined by means of tensile and impact tests.

EXPERIMENTAL

The poly(amino ether) (PAE) resin was kindly supplied by Dow Chemical (Midland, MI) under the trade name Blox. It has the following chemical structure:



It had a MFI of 9 g/10 min, measured at 200°C and with 2.16 kg load. According to the recommendations of the manufacturer, the polymer was dried at 65°C for 6 h in an air circulation oven before each processing cycle to minimize degradation reactions caused by moisture.

Extrusion was carried out at 200 and 230°C using a single-screw extruder (Brabender) driven by a Brabender PLE 650 plasticorder. The screw had a diameter of 19 mm, L/D ratio of 25, and compression ratio of 2/1. After each extrusion cycle, the extrudate was cooled in a water bath, pelletized and injection

molded in a Battenfeld BA-230E reciprocating screw injection-molding machine at a barrel temperature of 200°C and a mold temperature of 18°C. The screw had a diameter of 17.8 mm and L/D ratio of 17.8. The injection speed and pressure were 7.4 cm³/s and 2600 bar, respectively. Tensile (ASTM D-638, type IV) and impact (ASTM D-256) specimens were obtained. The PAE samples will be referred as 200PAE-1 to 200PAE-5 or 230PAE-1 to 230PAE-5 indicating the extrusion temperature and the number of passes through the extruder before injection molding. The virgin PAE pellets were also injection molded at 200°C as a reference material and are designated as PAE-0.

The MFI of PAE after reprocessing was measured with an ATS Faar extrusion plastometer at 200°C and with a 2.16 kg load. To check for the possible development of crosslinking reactions during melt processing, the kneading torque was measured in a Brabender batch kneader at 230°C and 30 rpm as a function of the residence time. The gel contents of the samples were determined by means of Soxhlet extractions. Approximately 7.5 g of the PAE samples were immersed in tetrahydrofuran (THF) for 90 h and then exposed to refluxing THF for 35 h. The gel content was calculated as the percent insoluble fraction relative to the initial sample weight. The infrared analyses were performed in a Nicolet Magna-IR 560 spectrophotometer with an attenuated total reflectance (ATR) objective. The samples were obtained from the injection-molded tensile specimens.

Dynamic-mechanical tests (DMA) were carried out using a TA Instruments Q800 DMA. A frequency of 1 Hz and a heating rate of 4°C/min from -110 to 120°C were used. The birefringence was measured at room temperature in an Olympus BX40 microscope equipped with a compensator. Each birefringence value was obtained from a minimum of three measurements.

Tensile tests were carried out with an Instron 4301 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 both unnotched and 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 reported value in both the tensile and impact tests.

RESULTS AND DISCUSSION

Color

Color changes after reprocessing can be important in some applications, mainly in the case of transparent polymers. A color change is also a first indication of degradation. In the case of PAE, and as observed in

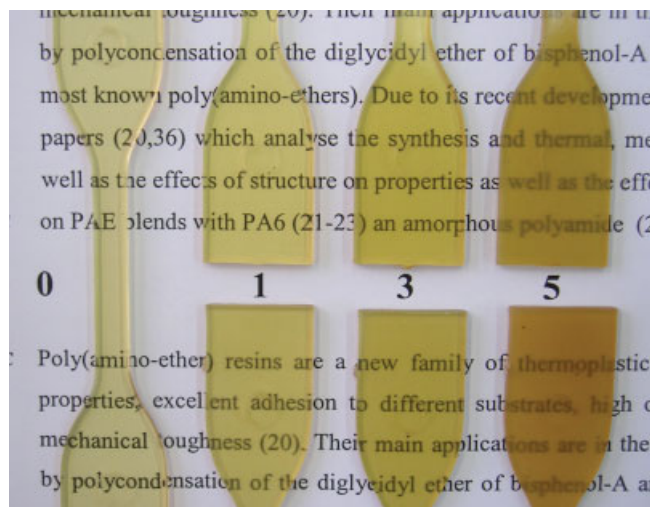


Figure 1 Tensile specimens of PAE, unreprocessed (0) and after 1, 3, and 5 reprocessing cycles at 200 (above) and 230°C (below). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 1, the original yellowish color darkened progressively with reprocessing, finally attaining an almost amber coloration. The influence of the processing temperature was slight up to three extrusion cycles, but after four and five extrusion cycles at 230°C, the specimens darkened. Transparency decreased slightly as the reprocessing conditions became harsher.

Chemical structure

The possible changes in the chemical nature of PAE due to reprocessing were tested by FTIR. The FTIR spectra of the virgin PAE (PAE-0), 200PAE-5, and 230PAE-5 specimens are shown in Figure 2. The absorption bands at ~ 1610 , 1510 , and 1460 cm^{-1} are attributed to the aromatic ring stretching vibration. The absorption band at 1230 cm^{-1} corresponds to the stretching vibration of the C—O bond of the ether groups, and that at 1030 cm^{-1} to the stretching vibra-

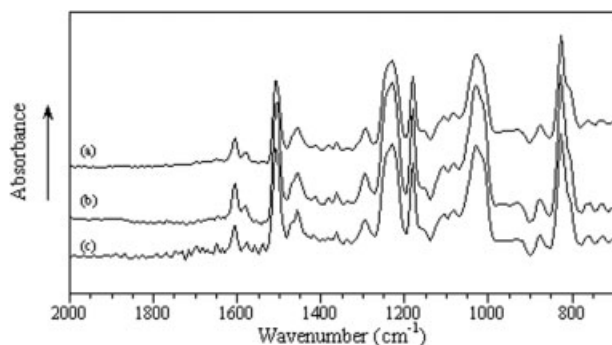


Figure 2 FTIR spectra of (a) PAE-0, (b) 200PAE-5, and (c) 230PAE-5.

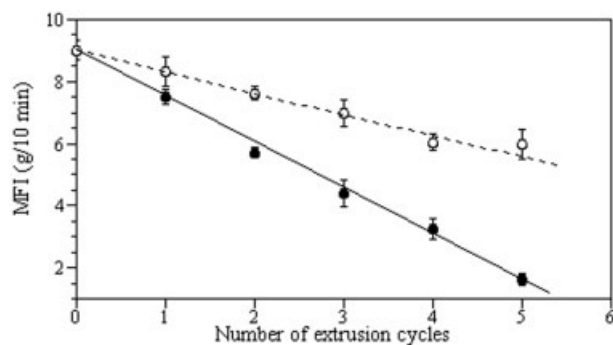


Figure 3 MFI of PAE reprocessed at 200 (white symbols) and 230°C (black symbols) as a function of the number of extrusion cycles.

tion of the C—O bond of the hydroxyl groups. Finally, the absorption band at 830 cm^{-1} is assigned to the C—H out of the plane bending vibration in the aromatic rings.

As can be seen, after reprocessing, the most characteristic bands of the spectra were almost unchanged and with similar peak height ratios. These results indicate that possible changes of the chemical structure of PAE, as they are not detectable by FTIR, would be very small. This apparently agrees with that found in most polymers^{2,12,15,18,20,34} where the chemical structure did not change with reprocessing.

With respect to possible changes in the molecular weight, they were tested by means of MFI measurements. As is known, the MFI allows an indirect analysis of the effects of degradation on viscosity and indirectly on the molecular weight. For this reason, the MFI of PAE was measured after up to five extrusion cycles for both extrusion temperatures and the results are shown in Figure 3. As can be observed, the MFI decreased continuously with the number of cycles, indicating a molecular weight increase. The MFI decrease and the molecular weight increase were more important after reprocessing at 230°C. This increase in molecular weight is unusual because, although the opposite has also been observed,^{16,35} a decrease in molecular weight is the usual result after polymer reprocessing.^{2,10,13,15,19,20} The increase in viscosity indicates that degradation takes place mainly through grafting and/or crosslinking, probably as a consequence of oxidative degradation; this is taking into account the experimental conditions associated with the test. As can also be seen, the decrease in MFI at 200°C is not the drastic decrease typical of the production of crosslinked products, and therefore testifies to grafting as the main degradation process. The grafting/crosslinking level, however, is likely to be low, because no change of the chemical structure appeared in the FTIR spectra (Fig. 2).

It has been reported³⁵ that thermal degradation of some polymers containing bisphenol-A moieties could

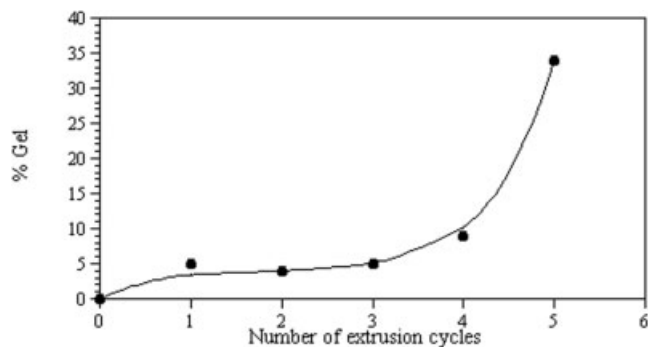


Figure 4 Gel content of PAE samples as a function of the number of extrusion cycles at 230°C.

be initiated at the isopropylidene group of the bisphenol-A units, and would be followed by chain scission or crosslinking. As PAE contains bisphenol-A units, this possibility was tested by kneading. On kneading, a continuous and strong torque increase was observed with time, indicating reactions. This continued up to attain a maximum, beyond which the torque decreased rapidly, producing a nonfusible insoluble powdery material, characteristic of crosslinking.^{31,36,37} This indicated that crosslinking in the melt state can occur in PAE. The exact nature of the reactions that give rise to crosslinking of PAE is unknown.

To gain insight into the possibility of crosslinking in the reprocessing conditions of this study, the reprocessed PAE samples were treated with THF in a Soxhlet extractor. PAE-0 and the samples extruded at 200°C were fully soluble, indicating the lack of crosslinking. Taking into account the MFI decrease, grafting reactions took place. In the case of the samples reprocessed at 230°C, a gel was obtained. This gel content is shown against the number of extrusions in Figure 4. As can be seen, the gel content was low up to three reprocessing cycles, but it then increased significantly to attain an approximate value of 35% after the fifth cycle. This result proves the existence of crosslinking after reprocessing at 230°C, and is consistent with the clear decrease in the MFI.

Physical structure

Degradation by grafting/crosslinking could affect the molecular mobility of the whole polymeric chain or of part of it. This change of mobility can be inferred from the glass transition temperatures (T_g) and the secondary transitions (T_β). For this reason, PAE and reprocessed PAE were studied by DMA. The maxima of the $\tan \delta$ -temperature peaks that correspond to the T_g were between 75 and 80°C and those corresponding to T_β were between -43 and -38°C. Although a slight tendency to increase in T_g and T_β after reprocessing was observed, the changes were less than 3 and 5°C,

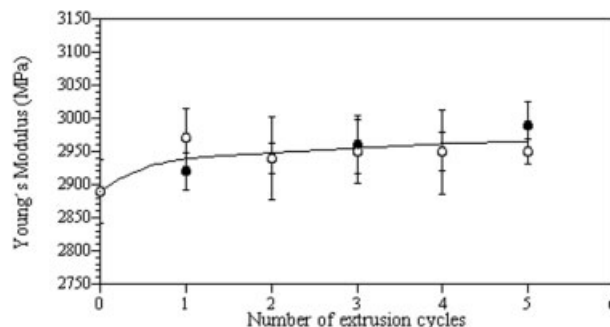


Figure 5 Young's modulus of PAE as a function of the number of extrusion cycles. Symbols as in Figure 3.

respectively. Thus, in spite of the partially grafted/crosslinked nature of the reprocessed PAE, reprocessing had no significant effect on the molecular and submolecular mobility of PAE. This also implies a low crosslinking density, even under the harshest reprocessing conditions, because a significant crosslinking level should lead to a detectable T_g increase.

Mechanical properties

The Young's modulus values of the samples reprocessed at 200 and 230°C are plotted against the number of extrusion cycles in Figure 5. As can be seen, although very slight, taking into account the standard deviation, a tendency to increase at the higher temperature could be detected. Provided this change occurred, it would be related with grafting/crosslinking reactions.

The yield stress of PAE against the number of reprocessing cycles is shown in Figure 6. As can be seen, the yield stress increased slightly with the number of reprocessing cycles, and to a greater extent at the higher temperature. The plot of the yield stress is usually similar to that of the modulus^{38,39} because both are related to stress and are measured at small deformations. Therefore, this yield stress behavior can be used to identify the tendencies difficult to detect in

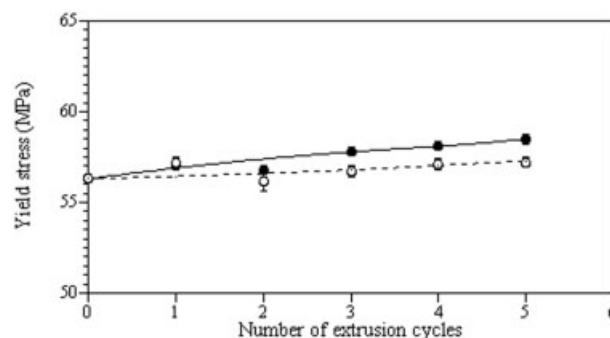


Figure 6 Yield stress of PAE as a function of the number of extrusion cycles. Symbols as in Figure 3.

Figure 5. Although some exceptions reporting slight increases^{2,34} or decreases^{2,20} exist, constancy in the small strain properties is the usual behavior of thermoplastics after reprocessing.^{15,18,20} A change in the small strain properties can be due to (i) densification due to a free volume decrease, (ii) a modification in the chemical nature of the polymer, or (iii) a change in the molecular orientation. When the specific volume of reprocessed PAE was measured, the change was negligible (maximum change: 0.2%), so that this parameter is not the reason for the modulus behavior. With respect to a change in the chemical structure, the small effect on modulus of grafting aid to the small grafting level leading to no changes in the modulus. The crosslinked products of degradation should lead to a modulus increase, but small because of the lack of changes in FTIR spectra. Moreover, the increase in the crosslinking level observed (Fig. 4) in PAE, reprocessed more than three times at 230°C, has no observable effect in Figures 5 and 6, as no curvature change was observed between three and four reprocessing cycles.

Finally, the orientation of PAE after reprocessing was estimated by means of birefringence measurements, and the results are shown in Figure 7. As can be seen, the birefringence, and consequently the orientation, increased slightly for PAE reprocessed at 200°C. The increase in birefringence was more noticeable for samples reprocessed at 230°C. Thus, the birefringence results agree with those of the small strain properties. The increases in orientation are attributed to the higher viscosity of the reprocessed PAE (Fig. 3). Therefore, the observed increases in small strain properties are mostly attributed to increased orientation caused by an increase in viscosity, and to a minor extent, to the degradation-induced reactions.

The ductility of PAE is represented against the number of extrusion cycles in Figure 8. As can be observed, ductility decreased particularly for specimens reprocessed at 230°C. The ductility decrease after five extrusion cycles was ~26% for PAE reprocessed at 200°C, and 44% after reprocessing at 230°C. However,

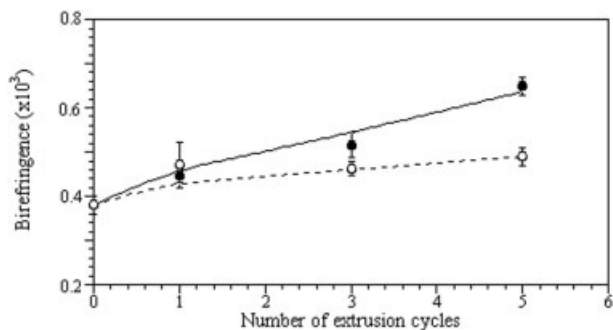


Figure 7 Birefringence of PAE as a function of the number of extrusion cycles. Symbols as in Figure 3.

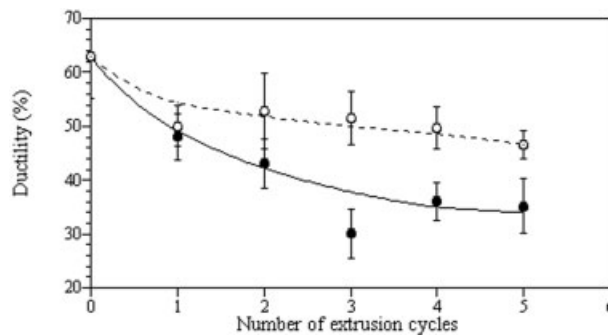


Figure 8 Ductility of PAE as a function of the number of the extrusion cycles. Symbols as in Figure 3.

as all the specimens yielded, PAE remains ductile nature even after harsh reprocessing. The reduced ability to elongate of grafted structures, and even more so for crosslinked ones after reprocessing at 230°C explains the observed decreases.

The break stress was almost constant with the number of reprocessing cycles at 200°C, and the decrease from zero to five reprocessing cycles at 230°C was only 2.5%. This was due to the fact that breaking in the tensile specimens took place always in the flat cold-drawing region of the tensile curves, and consequently the break stress was practically unaffected by changes in ductility.

The energy at break of PAE was measured by means of notched impact tests. The impact strength of PAE is very low and remained almost constant with the number of reprocessing cycles. This is different to the ductility behavior and 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 probably the most important reason is that the notched impact strength of PAE is very low (it is very notch sensitive), and therefore very little additional reduction can take place. Therefore, the different behavior of ductility and notched impact strength is attributed to the notched nature of the impact tests. This was also found in the reprocessing of PEI¹⁸ where reprocessing only affected the energy to initiate fracture. To prove this, unnotched impact tests were also done. The unnotched impact strength decreased after the first cycle, from 1200 to 550 and 350 J/m, respectively, for specimens reprocessed at 200 and 230°C, and then remained practically unchanged. This decrease is significant but similar to that obtained for other polymers.¹⁵ This unnotched impact behavior is similar to that of ductility, and indicates that reprocessing affects only the energy required to initiate the crack.

CONCLUSIONS

PAE darkened slightly upon reprocessing, viscosity increased, and some chemical reactions occurred, al-

though to a small extent. The reactions were grafting after reprocessing at 200°C and mainly crosslinking after reprocessing at 230°C. However, the mechanical properties scarcely suffered as a whole, and the performance of reprocessed PAE was maintained, which will probably not exclude most of its practical applications. This is because, although ductility decreased, PAE remained ductile, while constant or slightly increasing values were seen in the modulus of elasticity, yield stress, and notched impact strength. This was the case after five successive processing cycles at 200°C and also at 230°C, which is the highest temperature recommended for PAE processing. The changes in mechanical properties are attributed to some grafting/crosslinking and mainly to the increased viscosity-induced orientation.

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