The Tensile and Tear Properties of a Biodegradable Polyester Film

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Abstract: The tensile and tear properties of a biodegradable polymer, Biomax®, have been studied in order to assess this material in film applications. While the tensile strength of Biomax® was comparable to that of low-density polyethylene, the tear strength was found to be six times lower. A study of the load-displacement curves revealed a regular variation in load throughout the test, which was attributed to the presence of lower and higher strength regions in the polymer. The higher strength regions were characterized by the presence of polymer chains oriented parallel to the tear surface, while the lower strength regions were defined by an absence of molecular orientation and the presence of voids.

Keywords: Biomax®; Polyester; Tear strength; Tensile properties

INTRODUCTION

One approach to the problem of plastic waste management is the use of biodegradable polymers capable of degrading in soil conditions within months of disposal. The use of biodegradable plastics is particularly helpful when dealing with packaging waste. Biomax® is a commercial biodegradable polymer used in applications such as waste bags and

packaging. The material is based on poly(ethylene terephthalate) (PET) with propriety aliphatic monomers incorporated into the polymer. Biomax® degrades in soil by hydrolysis, facilitated by weak links inserted into the PET backbone chain.

Biodegradable polymers used in applications such as packaging must also possess good mechanical properties throughout their working life. For the current study, the tensile properties of Biomax® have been examined and compared. A comparison is made with low-density polyethylene (LDPE), which is commonly used in packaging applications. Packaging films require a high resistance to tear propagation while in use. The tear properties of Biomax® have also been investigated in order to establish the tear mechanism for this polymer. As molecular orientation within a sample is known to produce regions with different tensile and tear characteristics, samples from both machine and transverse directions were examined.[1–3]

MATERIALS AND METHODS

Materials

Biomax® sheets, approximately 30 μm in thickness, were supplied by Du Pont (Australia) Ltd. The films had been extruded, then blown with a blow-up ratio of 3. The films were provided in their original bubble configuration as two sheets joined at both sides. The width of the bubble was approximately 1 m and the length varied between 1 and 2 m. The processing directions of the film are shown in Figure 1, which illustrates the machine direction parallel to the side of the bubble and the transverse direction perpendicular to the machine direction. Commercial carry bags made of LDPE of 30 μm thickness were used for comparison purposes.

Tensile Testing

Tensile tests were carried out using an Instron 1022 Tensiometer fitted with a 2 kN load cell calibrated with a 500 N load cell according to the ASTM D882-95a method. Film strips (13 mm width × 60 mm length) were cut from sheets using a plastic template and scalpel. Samples were clamped in the instrument with a protective layer of paper. The upper crosshead was raised at a speed to produce an initial strain rate of $0.1 \, min^{-1}$. This parameter was kept constant for all experiments. The values reported are an average of a minimum of five measurements
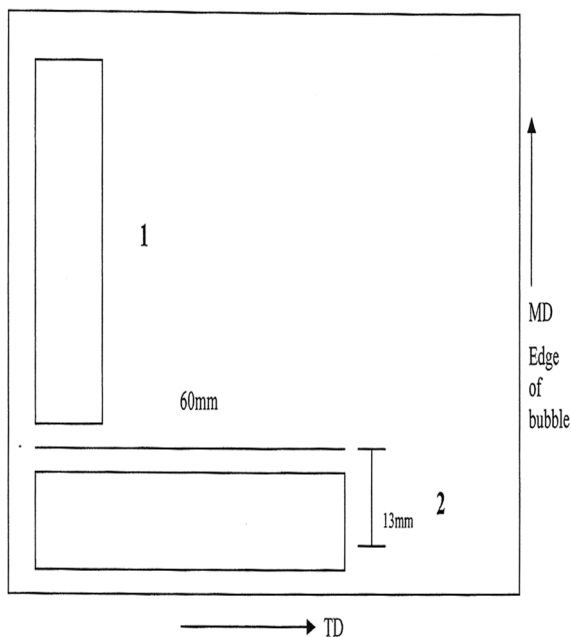
Figure 1. Processing directions in Biomax® film: (1) machine direction (MD); (2) transverse direction (TD).

for each processing direction, and the standard deviation is reported for the error value.

Tear Testing

The tear tests were carried out using an Instron 1022 Tensiometer according to the ASTM D81938-94 method. Specimens were removed from the sheet using a metal template (25×75 mm) and scalpel. A 500 mm slit was made halfway across one of the shorter edges of the film. Each leg of the trouser was placed in the tensiometer grips for testing. The values reported are an average of a minimum of five measurements for each processing direction, and the standard deviation is reported for the error value.

Scanning Electron Microscopy (SEM)

Samples were coated with carbon for SEM analysis and immediately examined after testing in order to minimize the extent of molecular relaxation.

All micrographs were collected using a JEOL 6300F FEG SEM. An accelerating voltage of 8 kV and a working distance of 15 mm were used for the collection of all images.

RESULTS AND DISCUSSION

Tensile Testing

The results of a comparison of the tensile properties of Biomax® and LDPE films are given in Table I. The tensile strength of Biomax® is comparable to that of LDPE. The breaking factor, the force required to produce failure across the width of the tensile specimen, was also similar for both polymer films. There is a significant variation for the percentage elongation across both types of films. The large variation in the percentage elongation at break was observed for the Biomax® samples investigated and reflects a difference in the assembly of the crystalline and amorphous regions throughout the film. Biomax® may consist of separate block regions containing terephthalate units and diacid units. These two phases are expected to possess different levels of crystallinity, similar to the hard and soft segments present in certain polyurethanes. The different degrees of crystallinity present in these two phases are likely to have a significant effect on the elongation at break. The yield elongation of Biomax® is approximately 30% lower than that of LDPE and is most likely due to the presence of the phenyl ring in the polymer backbone of Biomax®. Due to the rigidity of the phenyl unit, the movement of the adjacent carbonyl groups is restricted. In polymers with such a linkage, the entire system acts as a single unit, and, as a result, the p-phenylene linkage does not lie directly in the line of the chain, producing a zigzag structure.[4] This leads to increased crystallinity, and, as a result, the degree of elongation at break decreases. Further, the benzene rings within PET are capable of stacking together in an orderly fashion. This structural regularity also produces an increase in crystallinity, which again results in a lowering of the percentage elongation at break.

Table I.   Tensile properties of Biomax® and LDPE films

Property	Biomax®	LDPE
Tensile strength, kPa	9.5 ± 1.4	8.3 ± 2.0
Breaking factor, Nm^{-1}	438 ± 120	432 ± 134
Elongation at break, %	253 ± 152	417 ± 191
Elongation at yield, %	4.0 ± 1.2	6.6 ± 0.7
Tensile modulus	3.0 ± 0.6	1.4 ± 0.3

Hence, Biomax® is expected to yield at a lower elongation than LDPE, which contains no phenyl groups. The increased structural regularity of Biomax® is also reflected in the tensile modulus values. The increased crystallinity reduces the degree of elongation, producing an increase in the tensile modulus. The modulus determined for Biomax® is more than twice that observed for LDPE.

Table II lists the tensile properties of Biomax® samples taken from specific regions of the samples and processing directions. The tensile strengths of the samples taken from the machine direction are approximately 35% higher than those of samples taken from the transverse direction of the film. This variation is explained by the nature of the processing used to prepare the sample. The preparation of Biomax® blown film involves drawing the melt through an annular die and filling the sheet with compressed air to form a bubble. During processing the width of the bubble is subjected to a force from the compressed air; this is the only force that the transverse samples are subjected to during processing. However, the length of the bubble is also subjected to a drawing force as the sheet is drawn from the annular die, and, as a result, the polymer molecules are more likely to align together in this direction, making the regions more crystalline. Ziabicki[5] suggests that the orientation of the PET molecules is the primary structural factor responsible for the mechanical properties of the polymer. Hence, a greater tensile load would be required to fracture samples taken from the machine direction. A similar result was obtained by Crevecoeur and Groenickx,[6] who studied the effects of processing parameters on polyphenylene-ether/polystyrene films. Their study showed that tensile strengths for samples taken from the machine direction are up to three times greater than those of a sample taken from the transverse direction.

For the same processing direction the tensile strengths of Biomax® samples taken from the center of the film are approximately 40% higher that those of samples taken from the edge. This is a result of the changes to molecular alignment across the film. When the drawn melt is filled with compressed air, the center of the film, which is the upper and lower

Table II. Tensile properties of Biomax® from different specimen regions

Position	Processing direction	Tensile strength, kPa	Breaking factor, Nm^{-1}	Elongation at break, %	Elongation at yield, %	Tensile modulus
Edge	Machine	9.5 ± 0.9	365 ± 85	175 ± 68	4.4 ± 1.1	2.3 ± 0.4
Edge	Transverse	7.0 ± 0.6	254 ± 56	188 ± 73	2.6 ± 0.8	2.7 ± 0.2
Center	Machine	13.4 ± 1.1	655 ± 47	92 ± 47	4.0 ± 1.2	3.6 ± 0.6
Center	Transverse	9.7 ± 0.8	479 ± 52	101 ± 52	3.2 ± 0.7	3.3 ± 0.4

regions of the bubble, are exposed to a greater degree of stress. As a result, stress crystallisation is most likely to occur in these regions, resulting in higher tensile strength for samples taken from the center. A similar result was observed for the breaking factor, where an 80% increase was observed at the center regions, relative to film samples from the edge of the bubble. Again, this increase may be attributed to the increased degree of molecular orientation at the center of the blown film. A slight increase in the number of molecules present across a small sample width will produce significant changes to the tensile behavior. Table II also shows that there is a greater difference in properties for samples taken from different areas of the films than for those taken from different processing directions. This result suggests that a greater degree of anisotropy is introduced to the film by filling the bubble with compressed air than by the longitudinal extrusion of the melt from the die.

Tear Properties

Figure 2 illustrates the load-displacement curves obtained for specimens of Biomax® and LDPE. The tear strength of Biomax® is lower by a factor of approximately six than that of LDPE, making tear propagation more likely for Biomax®. The applied load of the Biomax® sample
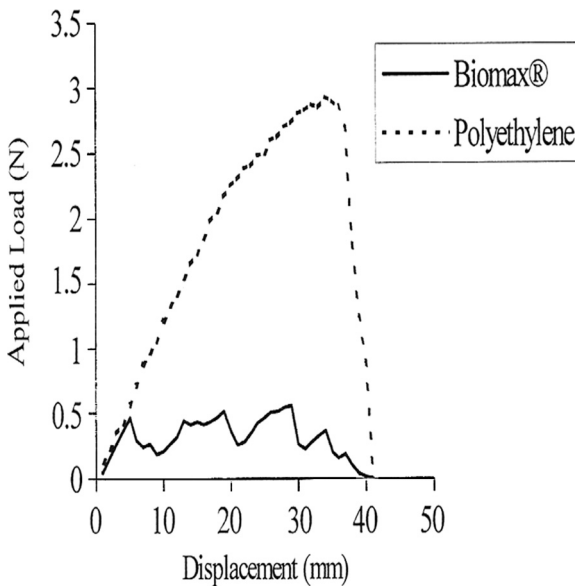
Figure 2. Load-displacement curves for Biomax® and LDPE films at 250 mm min^{-1}.

regularly decreases throughout the test after an initial loading of approximately 0.5 N. Decreases of more than 30% in the applied load are observed at every few mm of crosshead movement. For the LDPE film, the applied load gradually increased throughout the test and reached a maximum value just prior to catastrophic failure. These differences in the shape of the load-displacement curve demonstrate that the two polymers exhibit different failure mechanisms.

The observed tear behavior for Biomax® may be explained in terms of the morphological variation across the film. Two types of morphology appear to be responsible: fibrillar and void regions. Examination of the tear samples after testing using SEM showed evidence of fibrils (approximately 1 μm in width and 50 μm in length) aligned to the tear direction. In these regions, it is suggested that an alignment of the polymer chains has occurred, with the level of molecular orientation correspondingly increased. A greater force would be required to induce tear due to the fact that these regions are more crystalline. Secondary tears appearing perpendicular to the test direction were also observed. In these regions, very high applied loads would be required to produce a tear. These secondary tears propagate across more than 20 crystalline regions, cleaving several interphase boundaries before failure occurs. A considerable amount of energy would be required to produce such tears, and these areas are likely to be responsible for the increases in load observed throughout the tear test. The presence of fibrils in tear specimens of poly(butylene terephthalate) has been previously reported.[7] The second morphology observed for the Biomax® tear specimen is a region showing circular voids (approximately 0.5–2 μm) and no fibrillar structures on the tear surface. The voids appear regularly throughout the tear surface. The presence of voids indicates that these regions are more likely to tear at much lower loads than the fibrillar regions, where the polymer chains must be broken in order for failure to occur. Thus, when the tear propagates from a fibrillated region to these void areas, a decrease in the failure load occurs. The fact that the load decreases at approximately every 5 mm of cross-sectional head movement suggests that the void regions are distributed fairly evenly throughout the Biomax® film sheet.

The tear properties in machine and transverse directions were also considered, and samples from the center and the edge regions of the film were examined. Table III lists the tear strength values obtained for four different sample regions. Neither the processing direction nor the sample position has a significant effect on the tear strength. This contrasts with the tensile test results, which show that both these parameters result in notable changes to the tensile properties. However, the errors associated with the tear strength values are relatively high and reflect a lack of homogeneity throughout the Biomax® specimens. The speed at which this trouser test was carried out (250 mm min^{-1}) is a rate that may not allow

Table III. Tear strength of Biomax® films from different regions of the sheet

| Position	Processing direction	Tear strength, N
Edge	Machine	0.44 ± 0.10
Edge	Transverse	0.37 ± 0.06
Center	Machine	0.56 ± 0.20
Center	Transverse	0.52 ± 0.08

a significant degree of molecular orientation to occur during the tear process. Thus, the tear test results may merely reflect the strength of both the lower and higher strength regions. As a result, the load-displacement curves obtained for the Biomax® films from the four different regions regularly decrease throughout the tear test, similar to the results observed for the Biomax® specimen illustrated in Figure 2.

   In order to investigate the effect of test speed, tear tests were carried out on the machine edge samples using four crosshead speeds, and the results are given in Table IV. The tear strength increases as the crosshead speed is reduced, and a greater than threefold increase in the tear strength was obtained when the crosshead speed was reduced to 100 mm min^{-1}. At these lower speeds, there is more time for the polymer molecules to become oriented while under tension. Krishnaswamy and Sukhadia,[3] who analyzed the tear properties of linear LDPE blown films, found that the tear resistance increases when the crystalline lamellae are oriented close to the test direction. It was suggested that this high tear resistance occurred as a result of stress being dissipated along the long lamellae axes. Consequently, less energy is available for crack propagation, producing an increase in tear resistance. It is possible that a similar mechanism is occurring for Biomax®.

   Figure 3 illustrates the load-displacement curve of the tear test conducted at 100 mm min^{-1}. The load continually increases throughout the test until a maximum is reached just before failure. The curve shape

Table IV. Tear strength of Biomax® as a function of crosshead speed

Crosshead speed, mm min^{-1}	Tear strength, N
100	1.25 ± 0.24
200	0.81 ± 0.28
250	0.44 ± 0.10
500	0.35 ± 0.05
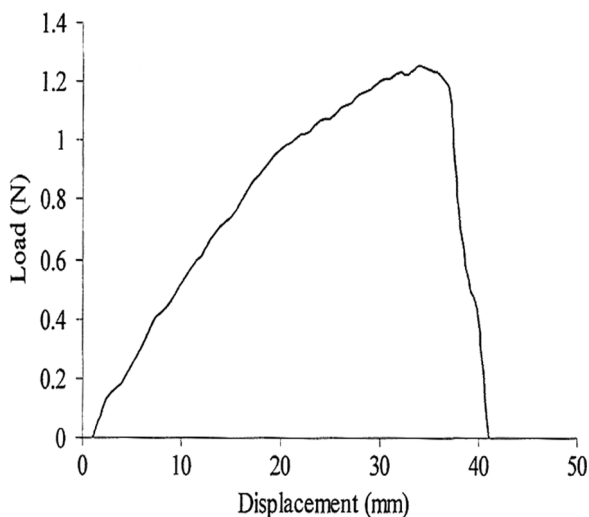
Figure 3. Load-displacement curve for Biomax® tested at $100 \, \text{mm} \, \text{min}^{-1}$.

suggests that a different tear mechanism operates at lower crosshead speeds. At a crosshead speed of $100 \, \text{mm} \, \text{min}^{-1}$, it appears that the lower strength regions of the Biomax® film are now able to support a higher load, so when the crosshead reaches these regions the load value is maintained. This suggests that the molecules within the lower strength regions align due to the tension applied during the tear test. If an increase in molecular alignment is occurring within the amorphous regions, then a greater degree of stress could be dissipated along the oriented chains, producing an increase in tear resistance. As a result, crack propagation would occur at higher loads in these amorphous regions.

CONCLUSIONS

The tensile properties were found to be significantly affected by the processing directions, with samples from the center of the film generally possessing superior tensile properties relative to those from the edge. The difference in tensile properties is attributed to the presence of residual stresses in the center regions. Trouser tear testing of Biomax® film showed that the applied load decreased at regular intervals throughout the test. A study of the tear morphology shows two distinct regions. The first region, which contains fibrils running parallel to the tear strength, is believed to be a region of high strength where the polymer molecules orient throughout the test. The second morphology, which contained voids, is believed to be responsible for the decreases in load

observed during the tear test. Tear tests carried out at different speeds indicated that the tear strength could be improved by increasing the degree of molecular orientation.

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