Interfacial Adhesion in Model Bioblends[*]

G. Biresaw,[1] C. J. Carriere,[1] and J. L. Willett[2]

[1]Cereal Products and Food Science Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University Street, Peoria, IL 61604
[2]Plant Polymer Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University Street, Peoria, IL 61604

ABSTRACT: Model bioblends were investigated for interfacial adhesion using the asymmetric double cantilever beam (ADCB) fracture method. The model bioblends comprised two synthetic polymer components, one of which was the nonbiodegradable polymer polystyrene (PS). The second component was a synthetic biodegradable polyester, which was either polycaprolactone (PCL) or Eastar Bio Copolyester® (EBU). The critical strain energy release rate (G_{Ic}) data from the ADCB fracture experiments on the model bioblends decreased in the order: PCL/PS > EBU/PS. This was opposite to the reported order in the interfacial tension of these bioblends. It is concluded that the relative interfacial adhesion of the model bioblends was due to better compatibility in PCL/PS blends over that in EBU/PS blends. © 2004 Wiley Periodicals, Inc.* J Appl Polym Sci 94: 65–73, 2004

Key words: asymmetric double cantilever beam fracture; bioblend; biodegradable polyester; interfacial adhesion; critical strain energy release rate

INTRODUCTION

Bioblends are polymer blends in which at least one component is a biodegradable/biocompatible polymer. The other component can be a biodegradable polymer or a nonbiodegradable synthetic polymer.

Biodegradable polymers could be of natural or synthetic origin.[1] Natural biodegradable polymers, also known as biopolymers, include carbohydrates (e.g., starch) and proteins. Agriculture based biopolymers have the added advantage of being renewable, that is, they provide unlimited sources of raw materials for bioblends. In addition, current oversupply of corn and other farm products have made ag-based biopolymers cost competitive relative to petroleum-based polymers.

There are a number of synthetic polyesters that are also biodegradable.[2] These biodegradable polyesters are synthesized using chemical and/or enzymatic methods. Examples of biodegradable polyesters include polylactic acid (PLA) and polycaprolactone (PCL).[2] Synthetic biodegradable polyesters are generally more expensive than natural biopolymers. However, biodegradable polyesters have excellent water-resistance properties, which make them desirable components for blending with biopolymers as well as synthetic polymers.

Bioblends allow the manufacture of materials with acceptable mechanical or other properties for the intended application, while at the same time being biodegradable and biocompatible. These properties make bioblends of great interest in the development of materials for a variety of applications, including packaging,[3] lubrication,[4] and medical devices.[5]

Investigation of bioblends for biomedical applications can be broadly categorized into drug delivery, implants, and cell culture/tissue engineering. In the area of drug delivery, bioblends are being investigated as mediums for the encapsulation and controlled release of a variety of implantable and nonimplantable formulations. Examples include: drugs for eye implants/treatment,[6] proteins,[7] insulin,[8] antitumor implants and drugs,[9] antibiotics and simple drugs,[10] anxiolytic and antidepressor drugs,[11] and vaccines.[12] In the area of implants, bioblends are being pursued in bone, orthopedic, and dental implants.[13–14] In the area of cell culture/tissue engineering, bioblends are being investigated for such applications as scaffolds for cell growth, storage, and delivery,[15–16] bioabsorbable sutures,[17] and tissue repair and transplantation.[18]

Bioblends can be classified into various categories, depending on the properties of the polymers being blended. The most widely studied bioblends comprise

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polymers that are all biodegradable. In these bioblends, at least one of the components is a natural biodegradable polymer, while the other is a synthetic biodegradable polyester. The natural biodegradable polymers used in these bioblends generally have poor water-resistance, but are abundantly available from renewable agricultural resources such as starch. On the other hand, the synthetic biodegradable polyester has excellent water-resistance properties. The goal is that of producing a bioblend with acceptable water-resistance and cost, while maintaining the biodegradability/biocompatibility of both blend components. These types of bioblends have been investigated for a variety of applications.[1–5,19–20]

Another type of bioblend comprises only synthetic polymers. In these types of bioblends, one of the components is a synthetic biodegradable polymer, while the other is a synthetic nonbiodegradable polymer. In these bioblends, the nonbiodegradable synthetic polymer provides the functional properties (e.g., mechanical properties) while the synthetic biodegradable polyester provides the required biodegradability and biocompatibility for the intended application. Such bioblends are of interest because they provide an opportunity for new application of "commodity" synthetic polymers in areas where some, that is, less than complete, degree of biodegradability and biocompatibility is acceptable for the intended application. In spite of their potential, there are a very limited number of investigations into the properties of these all-synthetic bioblends.[21–29] The work described in this paper is a continuation of our investigation into this important category of bioblends.

Successful development of all-synthetic bioblends requires that the biodegradable and nonbiodegradable synthetic polymers in the blend be compatible. Compatibility is a function of many properties of blends and blend components.[30–33] The factors influencing these properties, and eventually compatibility, are not fully understood. To help improve our understanding of the compatibility of all-synthetic bioblends, our group has initiated various studies on model blends.[24–29] In these model blends, polystyrene (PS) is used as the model nonbiodegradable synthetic polymer. The biodegradable synthetic polymer in these model blends can be any one of the following biodegradable polyesters: PLA, PCL, and Eastar Bio Copolyester (EBU).

Previous studies from our group on these model bioblends have focused on interfacial tension and tensile properties. Recently, we have extended our studies of all-synthetic bioblends by looking into the interfacial adhesion between PS and the biodegradable polyesters. This study was conducted using the asymmetric double cantilever beam (ADCB) fracture method.[34–45] ADCB was used to measure the critical strain energy release rate, G_{Ic}, of PS/PCL and PS/EBU model blends. This manuscript describes this study and relates the results to previous studies on the interfacial and mechanical properties of these model bioblends.

EXPERIMENTAL

Materials

Polystyrene (PS), polycaprolactone (PCL), and poly-(tetramethyleneadipate-*co*-terephthalate) known under the trade name Eastar Bio Ultra (EBU), were obtained from commercial sources and used as supplied. Table I lists the source of these polymers, along with available physical characteristics and chemical structures.

Compression molding

Compression molded polymers of size $127 \times 127 \times 3$ mm were prepared on a model 2518.0221 Carver Lab press (Wabash, IN) equipped with water-cooling system. The mold setup comprises a steel mold, two steel cover plates lined with a nonstick aluminum foil (Bytac®), and two larger and unlined steel plates. During molding the mold setup was first assembled in the press and preheated to the molding temperature.
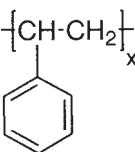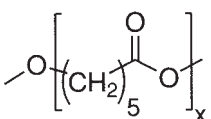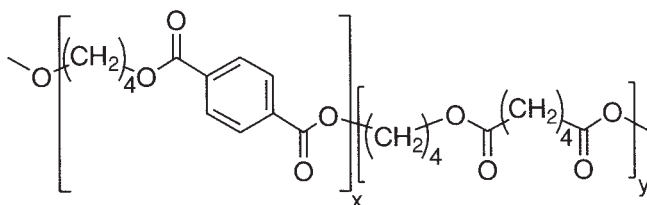
The press and mold assembly were then quickly opened, preweighed polymer sample added into the mold, quickly reassembled, and placed back into the press. The press was heated back to the mold temperature and held until the polymer melted completely (15–20 min). When complete melting was confirmed, pressure was applied (30–35 kpsi), and both temperature and pressure were maintained for 10 min. At the end of the 10 min, the heater was turned off, the cooling water was turned on until the press cooled to room temperature, the pressure was released, and the molded polymer removed. The weight of the polymers and the temperatures used in molding are summarized in Table II.

Welding of compression molded polymer pairs

Prior to welding, the compression-molded samples were cut into four equal-sized pieces using a precision CO_2 laser cutter (Laser Etch Technology, Buffallo, MN).

Polymer welding was conducted using model 2518.0221 Carver Lab press equipped with water-cooling system. The welding setup comprised a 6.37 mm thick steel mold, equipped with spring-loaded steel inserts to prevent the polymers from shifting during welding. The same cover plates used in compression molding were used during welding. A picture of the welding setup is shown in Figure 1. The welding procedure involved preheating the press to the weld temperature, and inserting the mold with the two

TABLE 1
Structure and Characteristics of Polymers Used in This Work

Name	Polystyrene	Polycaprolactone	PTAT[a]
Abbrev	PS	PCL	EBU
Comm Name	Styron 685D	Tone 787	Eastar Bio Ultra
Source	Dow	Dow	Eastman
Mn, Kg/mol	100[d]	80[e]	c
Mw, Kg/mol	280[d]	c	c
Tg, °C	100	−60	−33
Tm, °C	N/A	60	102–115
E$_Y$, MPa[b]	1271 ± 11	161 ± 1.2	35 ± 1.3

[a] Poly (tetramethyleneadipate-*co*-terephthalate).
[b] Ref 28
[c] Not reported
[d] Carriere, C. J., Biresaw, G, Sammler, R. L. Rheol Acta 2000, 39, 476.
[e] Shogren, R. L., Willett, J. L. Annu Tech Conf Soc Plast Eng 2001 59(2), 1860.

polymers on top of each other into press. The platens were then closed without any applied pressure, and heated until the weld temperature was reached. Then a slight pressure was applied, and the pressure and temperature maintained for 10 min. At the end of the 10 min, the heat was turned off, the cooling water was turned on, and the welded sample removed as soon as the press cooled to room temperature. The welding temperatures used in this procedure for PCL/PS and EBU/PS polymer pairs were 60°C and 104°C, respectively.

The welding temperatures were selected so that they were in the vicinity of the melting temperature (Tm) of the polyesters. Since welding involves applying small pressure to ensure intimate contact of the polymers, care must be taken to prevent polymer flow during this process, to avoid changes in the geometry or thickness of the specimen. Trial welding experiments were conducted at temperature starting 10–40°C below the Tm of the polyesters. In all cases, welding time was set at 10 min. These preliminary evaluations involved welding at the required temperature and visually evaluating adhesion.

For PS/PCL, preliminary experiments started at 52°C, which showed no adhesion. The welding temperature was gradually increased and adhesion was observed at 57°C and 60°C. A decision was made to conduct the ADCB study on the PS/PCL welds at 60°C.

For PS/EBU, trial welding experiments started at 60°C, where no adhesion was observed. Weak adhesion was observed at 66°C, which improved with increasing temperature. Based on the trial welding experiments, a welding temperature of 104°C was selected for conducting the ADCB study on PS/EBU welds.

TABLE II
Polymer Molding Data

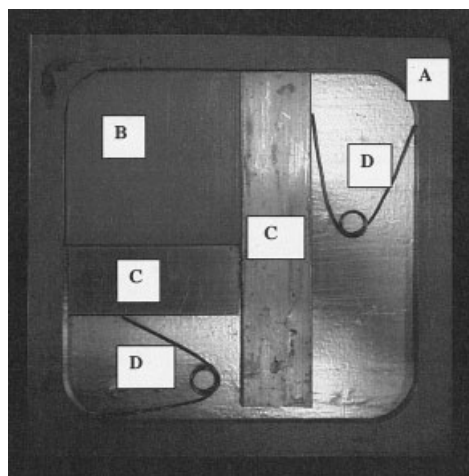| Polymer	Weight, g	Melt time, min	Molding temp, °C
PS	70	20	175
PCL	65	20	120
EBU	90	15	138

Figure 1 Polymer/polymer welding setup: mold (A); polymer to be welded (B); sliding barrier steel inserts (C); springs for pressing inserts against polymer (D).
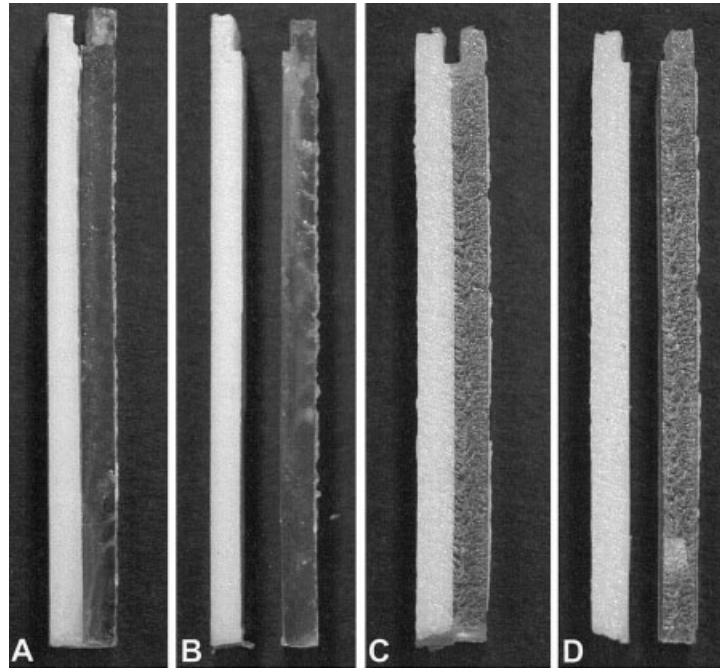
Figure 2 PCL/PS (A, B) and EBU/PS (C, D) welded specimen, before (A, C) and after (B, D) ADCB tests.

Preparation of specimens for fracture test

Specimens for the fracture tests were fabricated from the welded pieces as follows: First, the welded pieces were sliced into 9 mm wide specimen using a precision CO_2 laser cutter (Laser Etch Technology). A notch of 1.5 mm wide by 2.0 mm deep was then carved on one end of each specimen using the precision laser cutter. Pictures of specimen, before and after ADCB experiments, are shown in Figure 2.

Fundamentals of the ADCB method

The ADCB fracture method allows the estimation of interfacial adhesion between two polymers from measurements on samples obtained by welding the two polymers.[34–45] In conjunction with other methods, the ADCB fracture method can also be used to study the mechanism of de-bonding (e.g., chain scission versus pullout; adhesive versus cohesive) at the polymer/polymer interface.[34–45]

A typical ADCB procedure involves placing a wedge at the precracked end of the weld and measuring the crack length after crack propagation has stopped. The wedge could be a simple razor blade inserted manually or loaded from a mechanical testing machine such as an Instron Corp., Canton, MA. Studies by Brown et al. have demonstrated good correlations between the two wedging techniques.[34–38]

The ADCB fracture technique used in this work is illustrated in Figure 3. During the test, the wedge is pushed down into the notch at a slow speed, u. Contact of the wedge with the specimen introduces an applied force perpendicular to the direction of the wedge motion. The applied force pushes the two polymers apart and is opposed by the adhesive force. When the applied force exceeds the adhesive force, a "new" crack develops and the wedge movement is stopped. The crack propagates until equilibrium between the applied and adhesive forces is attained. When crack propagation is completed, the crack
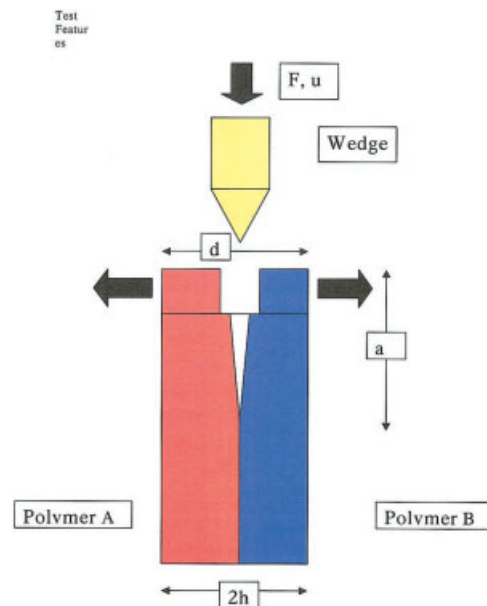

Figure 3 Basic concept of the ADCB fracture test.

length, a, and the separation distance, d, are measured and recorded. The wedge is then allowed to resume the downward movement, and the process is repeated several times on each welded specimen.

The interfacial adhesion between the polymers is estimated from the crack length, separation distance, and other polymer data, using the following equation:[43]

$$G_{Ic} = \{\tfrac{3}{16}[(d - 2h)^2 \, (Eh^3)]\}/\{a[1 + 0.64(h/a)]\}^4 \quad (1)$$

where:

G_{Ic}, critical strain energy release rate, J/m^2

$E = 0.5*[(E_1E_2)/(E_1+E_2)]$, Pa

E_1, E_2 are elastic moduli of polymers, Pa

d, separation distance at wedge, m

a, crack length, m

h, thickness of each polymer, m

G_{Ic} data obtained using ADCB procedure has been found to correlate with the degree of compatibility of blend components estimated using other techniques.[37,46] The method has also been found to be an effective tool in the investigation of the various factors affecting the performance of copolymer compatiblizers.[34–41]

As an example, Char et al.[37] used the ADCB fracture test to determine the effect of PS-*b*-PMMA compatiblizer on the interfacial adhesion between poly(phenylene oxide), PPO, and PMMA. Since PPO is known to be highly miscible with PS, it was predicted that the compatiblizer would result in improved fracture toughness of the PPO/PMMA blend. ADCB experiments showed that measured G_{Ic} values of the PPO/PMMA blend increased 60-fold when the compatiblizer was used. This improvement was attributed to improved interfacial compatibility brought on by preferential orientation of the diblock copolymer at the interface. The authors demonstrated this to be the case using dynamic SIMS analysis on fractured surfaces with deuterated diblock copolymers. The SIMS experiments showed that the diblock copolymer at the interface has reorganized so that its PPO block is predominantly on the PS polymer, while the PMMA block is predominantly on the PMMA polymer.

ADCB fracture tests

ADCB fracture experiments were conducted on Model MII TC-5–1068 Satec Servo-Hydraulic Fatigue Testing Machine (Satec Materials Testing Company, Grove City, PA). Key features of the instrument include: top and bottom hydraulic clamps with adjustable grip pressure; stationary bottom clamp, mobile top clamp; computer hardware and software for setting the speed and direction of top clamp movement; keyboard control of top clamp movement: start, stop, resume, stop, etc.; and computer data acquisition.

ADCB experiments were conducted using the following procedure: a razor blade was used to initiate a precrack of the interface at the notch of the specimen. The specimen was then mounted on the bottom clamp of the Satec, and the notch crack carefully aligned with the tip of the wedge mounted on the top clamp of the Satec. A traveling digital microscope (Model M1180–303LE Micrometer Slide with Linear Encoder, Gartner Scientific Corp., Skokie, IL) was zeroed by aligning the hairline to the top of the notch. Appropriate lighting and background were used to ensure proper viewing of the specimen interface through the microscope. The microscope was then lowered and focused at the end of the precrack. The wedge was manually lowered close to the notch, without touching the specimen. Using the keyboard command, the wedge was lowered at a rate of 0.1 mm/min, while keeping a watch on the crack through the microscope. Keyboard command was used to stop the movement of the wedge as soon as crack growth was detected. The hairline of the microscope was used to follow the growth of the crack over several minutes, and when crack growth stopped, the crack length was read off the digital display. The separation distance or the width of the specimen top at the wedge was measured to 0.001 mm using a digital micrometer (Model IP-54 Mitutoyo Digimatic Micrometer, Cole–Palmer Instrument Company, Vernon Hills, IL). Again, with the microscope focusing on the crack tip, the keyboard was used to initiate a downward movement of the wedge, and stopped as soon as crack growth was detected. The process is repeated 4–10 times on each specimen. At least four specimens were tested for each polymer pair weld. A picture of the ADCB fracture test setup, depicting the wedge, specimen, microscope, digital display, and lighting system, is shown in Figure 4.

RESULTS AND DISCUSSION

Evaluation of bioblends using ADCB fracture test

Separation distance, d, versus crack length, a, for welds of PS with PCL or EBU obtained using the setup shown in Figure 4, are plotted in Figure 5. The data in Figure 5 were obtained from tests on at least four welded specimens that were used to generate 4–10 data per specimen. As shown in Figure 5, the crack length increased with increasing separation distance, which was expected.

The data in Figure 5 along with the elastic moduli of the polymers (shown in Table I) were then used to calculate G_{Ic} using Equation 1. The resulting G_{Ic} data summarized in Figure 6 indicate a significantly higher interfacial adhesion between PCL and PS than that between EBU and PS.
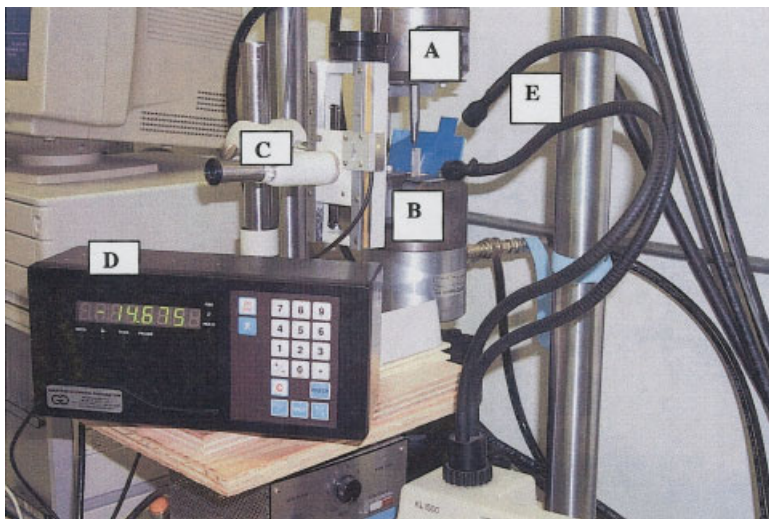
Figure 4 ADCB fracture test setup: top clamp and wedge (A); bottom clamp and specimen (B); microscope (C); digital readout (D); flexible lighting system (E)

Compatibility in bioblends

When polymers are blended, the resulting blend can be categorized into one of the following three types based on the degree of compatibility of the polymers in the blend:[47] (a) compatible, (b) incompatible, and (c) partially compatible. Compatible blends are those where the polymers are miscible in all proportions and at all temperatures. Compatible blends display strong intermolecular interactions and very small domain sizes. Incompatible blends are those that are immiscible or phase-separate at all proportions and temperatures. Immiscible blends display a morphology with large domains of one polymer dispersed in the other polymer, with no intermolecular interactions. Partially compatible blends are those that show compatibility in certain composition and temperature
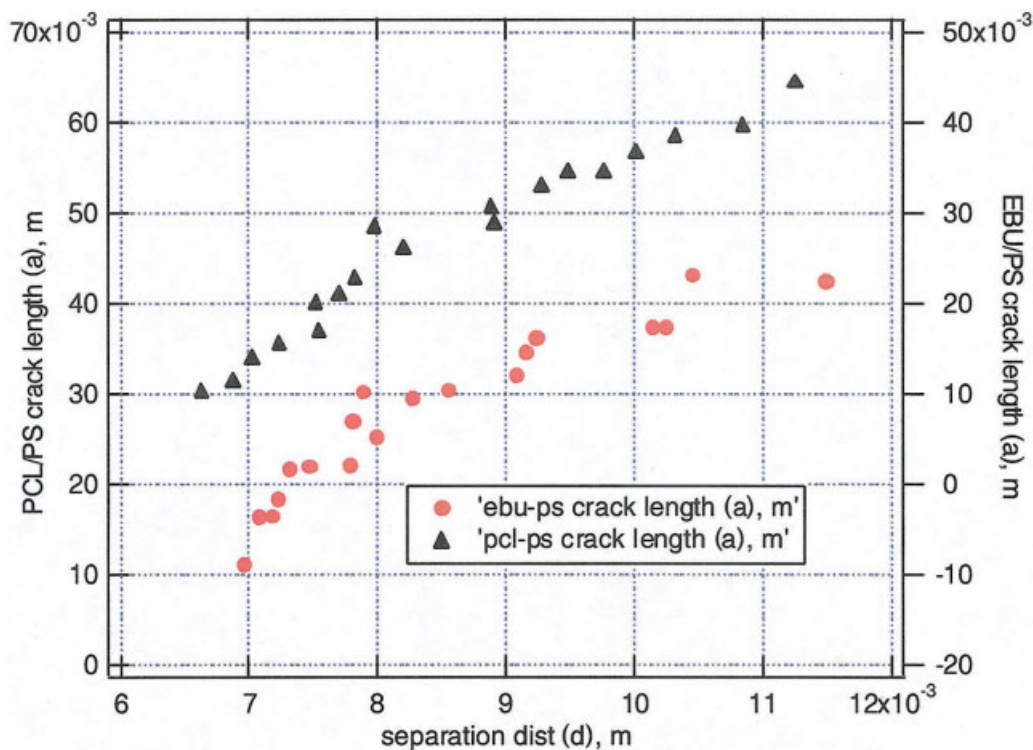

Figure 5 Separation distance versus crack length for PCL/PS and EBU/PS welds.
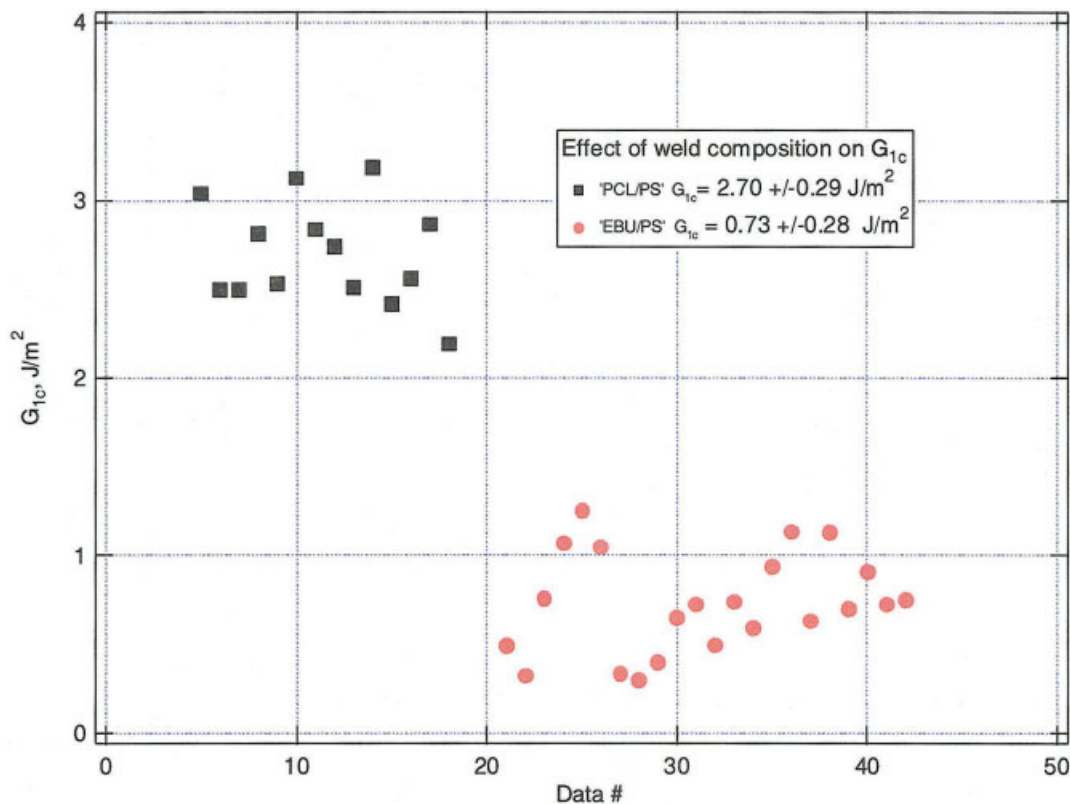
Figure 6 Effect of biodegradable polyester on blend G_{Ic}.

ranges. A variety of techniques are used to characterize the degree of compatibility of polymer blends including: thermal, mechanical, morphological, spectroscopic, and scattering. In general, improved degree of compatibility leads to smaller domain size, stronger interfacial adhesion, and improved mechanical properties.

Comparison of the G_{Ic} data from this study showed PCL/PS > EBU/PS (Fig. 6). This result indicates stronger adhesion of PS to PCL than to EBU. One reason for the observed trend in G_{Ic} could be the differences in the degree of compatibility in PCL/PS versus EBU/PS blends. Improved compatibility will result in stronger adhesion and, hence, higher G_{Ic} values.[46–48] The observed G_{Ic} data will indicate better compatibility of PCL/PS blend over EBU/PS blend.

One of the factors that affect polymer blend compatibility is interfacial tension.[30] Improved blend compatibility should be reflected in lower interfacial tension. Thus, if the observed G_{Ic} from this study is due to better compatibility of PCL/PS over EBU/PS, it should be reflected in the relative interfacial tensions of these two blends.

The interfacial tension of polymer blends can be determined indirectly from polymer properties (such as surface tension, solubility parameter) or directly using equilibrium or dynamic methods.[31–33] Techniques that allow for a direct measurement of interfa-

cial tensions using dynamic methods are the most preferred. These techniques allow for the measurement of the interfacial tension of high molecular weight and high viscosity polymer blends in a relatively short period of time without complication from polymer degradation. One such technique is the imbedded fiber retraction (IFR) method,[49–50] which has been used to measure the interfacial tension of a number of high viscosity blends.[29] The IFR has been used to measure the interfacial tension of the PCL/PS and EBU/PS blends used in this work,[26–27] and the results are compared with the G_{Ic} data from this work in Table III. As can be seen in Table III, these blends showed interfacial tension data that increased in the order PCL/PS < EBU/PS, which is the exact opposite

TABLE III
Comparison of Interfacial Adhesion and Interfacial Tension of PCL/PS and EBU/PS Blends

Property[a]	PCL/PS	EBU/PS	Comment
G_{IC}, J/m^2	2.70 ± 0.29	0.73 ± 0.28	This work[b]
IT, dyn/cm	7.6 ± 1.8[c]	12.6 ± 2.8[d]	IFR method

[a] Abbreviation: IT, interfacial tension.
[b] Total of 4 specimens for each blend; each specimen tested 4–10 times.
[c] Ref. 26.
[d] Ref 27.

of the order of G_{Ic} data obtained in this work. The interfacial tension and the G_{Ic} data shown in Table III give a strong support to the suggestion mentioned earlier that the relative G_{Ic} data observed in this work could be due to differences in the compatibilities of these two blends. Similar trends between the interfacial adhesion and interfacial tension of polymer blends have been reported by others.[35–36,46]

SUMMARY AND CONCLUSION

Bioblends comprising all-synthetic polymer ingredients allow the development of biodegradable and biocompatible materials from "commodity" synthetic polymers. In these blends, the biodegradable polyester component provides the required biodegradability and biocompatibility, while the commodity synthetic polymer provides the needed mechanical or other required property at a competitive cost.

Successful development of all-synthetic bioblends requires that the biodegradable polyester and the commodity polymer be compatible. Compatibility is essential for producing bioblends that meet the required mechanical and other properties for the intended application.

In this work, the interfacial adhesion of model bioblends was investigated using the ADCB fracture method. The model bioblends were PS/PCL and PS/EBU. The ADCB fracture method allows the estimation of interfacial adhesion between two polymers from measurements on samples obtained by welding the two polymers. From these measurements, G_{Ic} is calculated. G_{Ic} is directly proportional to the interfacial adhesion between blend components.

The bioblends investigated in this work showed G_{Ic} data decreasing in the order PCL/PS > EBU/PS. Previously measured interfacial tensions of these bioblends decreased in the exact opposite order. These interfacial tension results predict better compatibility of the PCL/PS blend over the EBU/PS blend. Thus, the observed order of the interfacial adhesion data from this work is best explained in terms of improved compatibility of the PCL/PS blend over the EBU/PS blend. Improved compatibility is one of many factors (e.g., cost) that are considered when selecting bioblend components for various applications. It appears that, all factors being equal, PCL will be the preferred candidate over EBU for the development of all synthetic bioblends with polystyrene.

Even though the interfacial adhesion results from this work showed trends that were consistent with previously measured interfacial tension of the same blends, the underlying reasons for this phenomenon is not clear. Understanding this will require, among other things, knowledge of the intra- and intermolecular interactions of the polymers in the blend. Various approaches for understanding polymer interactions in bioblends are currently being pursued by our group.

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