Polylactide Copolymers: Effect of Copolymer Ratio and End Capping on Their Properties

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ABSTRACT: Racemic copolymers of polylactic acid were investigated to determine the effect of copolymer ratio on melting point, degree of crystallinity, mechanical properties, and processing behavior. The copolymer ratio was found to have a strong influence on the crystallization behavior of the polymer. In addition to the ratio of the L-form to a random mixture of the D and L forms of the lactic acid in the copolymer, the effect of the polymer's molecular weight was examined. The copolymers were produced from the lactide form of the monomer to achieve weight average molecular weights above 100,000. The molecular weight had a profound influence on processability and rate of crystallization. Other notable factors influencing the properties and processing of the copolymers were the concentration of residual monomer in the polymer, the processing time-temperature history, and the extent of molecular weight degradation during processing. An important factor in the commercial development of biodegradable polymers is the ability to control the rate of degradation. Ideally, the polymer should not degrade during functional use, but degrade quite rapidly when discarded. This paper discusses various aspects associated with the control of the rate of degradation of polylactide copolymers; both from the perspective of stabilizing the polymer during processing and product use, and subsequently accelerating the rate of degradation after disposal. Of particular interest are the influences of molecular weight, crystallinity, end capping, and plasticization. © 2005 Wiley Periodicals, Inc. Adv Polym Techn 24: 69–82, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/adv.20032

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Introduction

While the most common approach to reducing the volume of plastics in the waste stream is recycling, a major requirement for recycling to be successful is the existence of a large source of minimally contaminated single-identity material. Large-scale separation, cleaning, and sorting combine to form significant roadblocks to economically competitive recycling. At the same time there are numerous packaging materials that consist of multiple layers of quite dissimilar materials. One significant example is plastic-coated paperboard, particularly when an aluminum coating has been applied. Such packaging materials also contain printing inks, and the paper is often highly filled with clay. Collecting, dissembling, and separating such materials has not proven to be economically viable. Such products clearly represent a potential opportunity for biodegradable polymers.

In the consumer market, disposable fast food, dairy and delivery containers, food serviceware, medical garments, and waste bags have also been identified as potential markets for biodegradable plastics. Other needs for biodegradable plastics include compost bags, coatings for seeds, pesticides, and fertilizers, as well as agricultural mulch films for timed release of pesticides and fertilizers. The potential market for biodegradable polymers is small compared with the overall plastics market, and a significant portion of it is targeted for agricultural applications rather than disposable packaging.

Many biodegradable polymers have been investigated including cellulose acetate, polycaprolactone, polyesteramide, polyglycolide, polyhydroxyalkanoate, polylactic acid, polyvinyl alcohol, and starch-based polymers. Serious candidates include starch-filled polyethylene and polyhydroxybutyrate. The former is opaque and not suited as a clear overcoat, but it has already found markets in disposable garbage bags and agricultural films. The second material is currently too expensive to compete as a discardable packaging film. A polymer candidate that meets the requirements of a biodegradable, clear packaging film as well as those of an agricultural film is polylactic acid (PLA), also known as polylactide (similarly designated PLA for reasons that will become obvious shortly).[1–5]

PLA was originally developed as a resorbable polymer for the controlled release of drugs in biomedical applications. PLA is still under development for further use in medical applications; e.g., as sutures, ligament replacements, resorbable plates and screws in fracture fixation (i.e. in orthopedic repairs), controlled drug release carriers, and arterial grafts. Controlled hydrolysis and breakdown into lactic acid makes PLA ideal for applications in which its eventual absorption into the body is desired. The same characteristics that make PLA appropriate ideal for medical applications make it a good candidate for environmentally degradable plastics. While cost is secondary to performance in medical applications, it is of primary importance in disposable packaging applications.

It is important to recognize that PLA is among the class of polymers known as polyesters. Polyesters are among the most versatile classes of polymers. Aliphatic, linear polyesters usually have low transition temperatures, which make them useful as plasticizing agents. Linear aromatic polyesters have higher transition temperatures, thus making them useful as fibers, films, and molded objects. PLA is a linear aliphatic polymer, but its major transition temperatures are above room temperature. Its ability to develop attributes associated with the aromatic polyesters is due to the relative rigidity of its side groups. In many respects PLA has characteristics similar to the most well-known aromatic polyester, polyethylene terephthalate, PET. Both can be thermally quenched from the melt to prevent crystal formation. Amorphous unplasticized PLA resembles clear polystyrene, provides good aesthetics (gloss and clarity), but it is stiff and brittle, and consequently needs modification for most practical applications (i.e. plasticizers and/or copolymerization to increase its flexibility). Both PLA and PET can be oriented, strain crystallized, and heat set to produce tough strong, clear fibers or films.[6] Both polymers can be copolymerized to control the ultimate level of crystallinity achieved by annealing, or orienting and heat setting. The major difference is that PET has a glass transition temperature of 80°C and a melting point of 255°C, while 100% linear PLA has a glass transition temperature of 55°C and a melting point of 178°C. With appropriate modification, PLA can have properties

similar to a wide range of commodity polymers, including polyethylene and polypropylene.

A unique advantage of PLA is that the basic raw ingredient comes from corn, a very abundant crop, and a renewable resource. Cornstarch is first converted to dextrose, which is fermented to lactic acid. Wheat, maize, sugar beet, and agricultural wastes have also been used as the starting feedstock. The chemical structure of lactic acid is

$$CH_3-C(OH)H-COOH$$
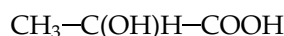
Lactic acid has two optical isomeric forms or enantiomers. The L-enantiomer occurs in nature, while a 50/50 D,L racemic mixture results from the synthetic preparation of lactic acid. The pure L-lactic acid is the more valuable entity, being worth nearly three times as much the mixture of L- and D-lactic acids. Low molecular weight polylactic acid is made by direct polymerization of L-lactic acid. Either form of lactic acid can be copolymerized with the other enantiomeric form, and both forms can be copolymerized with other monomers. For example, polylactic acid has been copolymerized with glycolic acid, ethylene glycol, caprolactone, and ethylene oxide.[7]

Lactic acid can be polymerized by a stepwise reaction process to form a low molecular weight polymer ($M_w < 20,000$). That reaction, shown below, provides an indication as to the hydrolytic instability of the polymer.

$$n\{CH_3-C(OH)H-COOH\}$$
$$\Leftrightarrow -(CH-COO)_n- + nH_2O$$
$$| $$
$$CH_3$$
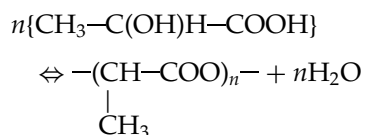
The reaction is reversible. To produce the polymer, water is drawn off by vacuum, driving the reaction to the right. The structure of the polymer permits it to readily absorb water, however, thus driving the reaction back to the monomer. Lactic acid is reduced to water and carbon dioxide by a wide number of bacteria. PLA is absorbed by the body, where it is chemically reduced to the same small molecules.

If a higher molecular weight polymer is desired, the low molecular weight material can be thermally unzipped to generate lactide (3,6 dimethyl-1,4-dioxane-2,5dione), whose chemical structure is[8,9]
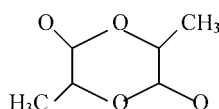
Lactide is not readily available as lactic acid, but has the distinct advantage of polymerizing to a much higher molecular weight. Some investigators even refer to the high molecular weight polymer made from lactide as polylactide, confining the name polylactic acid to the low molecular weight entity. Both have the same chain structure, however. A quick look at the structures of lactic acid, lactide, and the resulting polymer reveals that a simple ring opening reaction is all that is needed to produce PLA from lactide, while a transesterification reaction is needed to produce the polymer from lactic acid. The most effective way to create the high molecular weight polymer is to convert lactic acid directly to lactide. The lactide is then purified through vacuum distillation. The lactide ring also has two enantiomeric forms resulting in the L- and D-isomers.

The polymer formed from 100% L-polylactide is highly crystalline, and has a melting point of 178°C. Copolymers made from a random mixture of 50% L- and 50% D-lactide are amorphous. Crystallinity does not develop under normal thermal processing until the percentage of L- in a L-/D,L random copolymer exceeds 85%. Table I shows the effect of L-concentration on the thermal characteristics of a series of (L-/D,L) random copolymers. Note that the range of the glass transition temperatures of the polymers is narrow, between 55°C and 63°C. The amorphous form of the polymer has Vicat softening point of only 50°C. The heat distortion temperature can be increased by introducing crystallinity, and more significantly by orienting and heat setting the crystalline form of the polymer.

Control of PLA crystallinity is important not only to raising the maximum temperature utility of the polymer, but also to its degradation time. Crystalline poly(L-lactide) is more resistant to hydrolytic degradation than the amorphous random L-, D-copolymer

TABLE I ■
Primary Transition Temperatures of PET and Selected PLA Copolymers

Copolymer Ratio	T_g (°C)	T_m (°C)
PET	80	255
100/00 (L-/D,L) PLA	63	178
95/05 (L-/D,L) PLA	59	164
90/10 (L-/D,L) PLA	56	150
85/15 (L-/D,L) PLA	56	140
80/20 (L-/D,L) PLA	56	(125)[a]

[a]Melting point achieved by strain crystallization.

form. Suture materials requiring long holding times are typically higher in L-content than those intended for rapid absorption. Molecular weight is also a significant factor in the durability of the polymer. The composition of the copolymer ratios also results in different mechanical properties when processed by different means.

This paper examines the thermal, rheological, and mechanical property characteristics of a number of (L-/D,L)-PLA copolymers. A major consideration in analyzing these polymers was the effect of a molecular weight that changed during the various processes to which the polymer was subjected. An important feature in the use of polylactide polymers is the ability of the polymers to maintain their base properties until discarded and then degrade as rapidly as possible. There are a large number of ways to control the degradation of polylactide polymers. This paper will describe qualitatively a number of them and provides experimental data demonstrating the effects of a few of the most important. These polymers were all thermally processed, either by injection molding, extrusion, or thermoforming. In many cases they were annealed after processing.

Degradation Mechanism and Control

As mentioned above, polylactides belong to the class of polyester polymers. As such, the primary degradation mechanism is hydrolytic breakdown, resulting in repeated reductions in molecular weight, until only microbial digestible low molecular weight oligomers remain. The degradation process goes through a number of distinct and observable stages. These can be summarized as follows:

- absorption of water into the polymer;
- hydrolysis resulting in molecular weight breakdown, associated with an accompanying loss in mechanical properties;
- continued hydrolysis resulting in opacity;
- loss of mechanical integrity;
- reduction in volume as smaller molecular weight species are consumed by microorganisms and converted into carbon dioxide and water—microorganisms have been shown to consume oligomers having a molecular weight less than 1000.[10]

In many respects, the degradation process accelerates as it proceeds, due to the fact that each hydrolytic reaction creates two new end groups. These end groups polarize the ester bonds and serve as attracting points for additional water absorption. This process suggests that if the polymer is suitably stabilized it can remain functional for quite some time as a product, but when subjected to a degrading environment it will begin to degrade at an ever increasing rate.

The possible approaches to controlling the rate and occurrence of degradation include[11]:

- adding an activator;
- adding a water absorber;
- coating the part with either a hydrophobic or hydrophilic material;
- stressing the part;
- crosslinking the polymer;
- copolymerizing the PLA;
- modifying the molecular weight;
- controlling crystallinity;
- end capping the polymer chains;
- plasticizing the polymer.

Activators include acids that naturally attack PLA by polarizing the ester groups and attracting water into the polymer. Bases that produce hydroxyl ions when exposed to water also act as activators. Moisture absorbing materials include silica, talc, various clays, etc. These materials are strong water absorbers and accelerate the ingress of water into the polymer. Hydrophobic coatings can retard moisture ingress and preserve the part during use. Hydrophilic coatings can attract moisture and hasten attack.

As discussed previously copolymerization is a very effective means for controlling or eliminating crystallinity. Crystalline polymers degrade much more slowly, as the crystals are not easily attacked. In addition, the chemical attack of amorphous polymers can be accelerated by mechanically stressing the part, while similar stressing has less of an effect on semicrystalline polymers.[12]

Plasticization not only changes the physical properties of the polymer, making them softer and more pliable, but opens the internal structure so that when degradation begins the plasticizer can leach out and allow moisture to quickly permeate into the structure of the polymer.

Lower molecular weight polymers degrade more quickly than higher molecular weight polymers.

Crosslinking the polymer introduces three-dimensional chain linkages that effectively reduce the rate of degradation.

End capping has several effects on the degradation of PLA. PLA degrades by several mechanisms; random scission within the polymer and backbiting of the terminal hydroxyl ends. Moreover, the carboxyl ends promote degradation by polarizing ester bonds and providing acid groups that accelerate the rate of hydrolysis.[13] The carboxyl groups attract and become surrounded by water molecules that promote degradation. As more carboxyl end groups are formed during hydrolysis, additional acid groups are formed that trap and accumulate more water. End capping both ends of the molecule reduces water absorption at the molecule's natural hydroxyl and carboxyl ends. This reduces the degradation rate until the polymer is exposed to degradation conditions. Subsequent chain scission accelerates the rate of degradation by continually introducing new hydroxyl and carboxyl chain ends.

The reactive hydroxyl groups are more responsible for degradation during melt processing, a situation that can lead to unwanted color formation. One way to prevent this is to end cap the hydroxyl groups with acetic anhydride. Free carboxyl end groups are more responsible for degradation after the part has been made, and during subsequent disposal. Carboxyl end groups are end capped after the polymer has been synthesized. Diazomethane is a typical carboxyl end cap.

The most useful of the above techniques, given that the majority of intended applications are as films or coatings, control of crystallization, by either processing or copolymerization; control of molecular weight; end capping; and plasticization.

Sample Preparation

The polymers investigated in this study were made in a pilot plant batch reactor directly from lactide. As such, they all have high molecular weights, although the molecular weights varied among individual runs. The lactide monomer was contained and constantly stirred under a dry nitrogen blanket at temperatures between 150°C and 200°C. The catalyst used was 0.02 pph stannous octoate. Typical reaction times were 20 h for the batch reaction. Complete synthesis details can be found in Sinclair.[14] Samples were prepared for analysis either by extruding the polymer into films or by injection molding

into test bars. Some of the extrusion was done on a Baker–Perkins tandem 30 mm diameter extrusion system. This system consisted of a vented co-rotating twin screw section (11:1 L/D) feeding a single screw (20:1 L/D) melt pump. The extruded 12 cm wide film was quenched on a water-cooled chill roll. The thickness of the extruded film varied, but was on the order of 0.25 mm thick. During extrusion the maximum polymer temperature was always less than 200°C. A maximum temperature of 190°C was the control target. Residence times in the extruder were on the order of 1–2 min. Extrusion was also done on a Berstorrff 40 mm diameter co-rotating twin screw extruder (35:1 L/D). This machine also had venting capability, close temperature control, and the ability to produce film up to 25 cm wide and 2.5 mm thick. It also had comparable residence times to the Baker–Perkins extruder.

Samples of extruded film were biaxially oriented, 3× by 3× at 85°C, on an E. M. Long machine. Both oriented and unoriented films were thermoformed on a single station lab thermoformer using infrared heat and vacuum forming pressure. Thermoforming temperatures were varied to study the effect of temperature on forming detail.

Injection molding was done on a 75 ton New Britain machine. Standard 3 mm thick tensile and flex bars were molded at 190°C. The polymer was injected into both a cold (10°C) mold, as well as a heated (50°C) mold.

Effect of Copolymer Ratio on Crystallinity

Thermal analysis was performed on a Perkin–Elmer DSC-7 system. All samples were analyzed under nitrogen at 10°C/ min heating rates. The T_g and T_m of polylactic acid polymers depend on the copolymer ratio of L- to D,L, the molecular weight of the polymer, and the amount of monomer remaining in the polymer. The effect of copolymer ratio on the key transition temperatures of monomer free, high molecular weight PLA copolymers is shown in Table I. Copolymerization has a greater effect on the melting point than the glass transition temperature. The glass transition temperature quickly reaches a constant value when the concentration of D,L in the copolymer reaches 10%. The melting point continues to drop as the D,L content increases. Above 15% D,L the polymer is essentially amorphous, and, thus, has no melting point.

POLYLACTIDE COPOLYMER PROPERTIES

Relatively low molecular weight (100%L-)PLA can have a crystalline content as high as 85%.[13] This makes the polymer very rigid and brittle at room temperature. Undesirable brittleness exists even in the higher molecular weight polymer. Figure 1 shows the DSC curve for (100%L-)-PLA, with its transition temperatures clearly distinguished, and no evidence of a crystallization exotherm. Had this material been rapidly quenched from the melt, it would have been vitrified in the amorphous state. (100%L-)PLA, like PET, has a finite crystallization half-life. The crystallization half-time increases as the degree of copolymerization increases. Copolymerization of the L-enantiomer with the D,L enantiomer also reduced the maximum degree of crystallinity attainable, making the polymer less brittle, and enhancing its toughness. There is a limit as to the degree of copolymerization that is practical, however. An 80/20 copolymer has such a long crystallization half-time that for all practical purposes it cannot form crystals by thermal processing, and is therefore, usually amorphous. Figure 2 shows a DSC curve of two samples of 80/20 (L-/D,L)PLA. The lower curve shows only a glass transition temperature, with no evidence of crystallization potential. The upper curve shows a crystalline melting peak at 125°C. This sample was strain crystallized and will be discussed in detail later. Note that the peak height of the crystallization endotherm is quite small compared to that of the other crystallizable PLA polymers. Since the amorphous 80/20 copolymer has a glass transition temperature only 33°C above room temperature, its practical utility is limited. Only when the
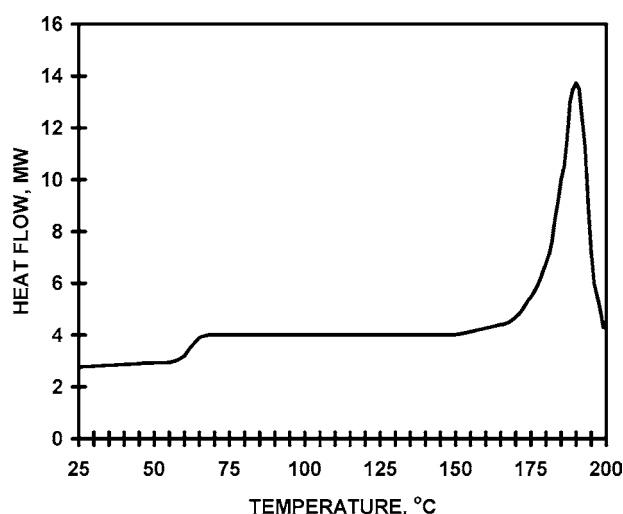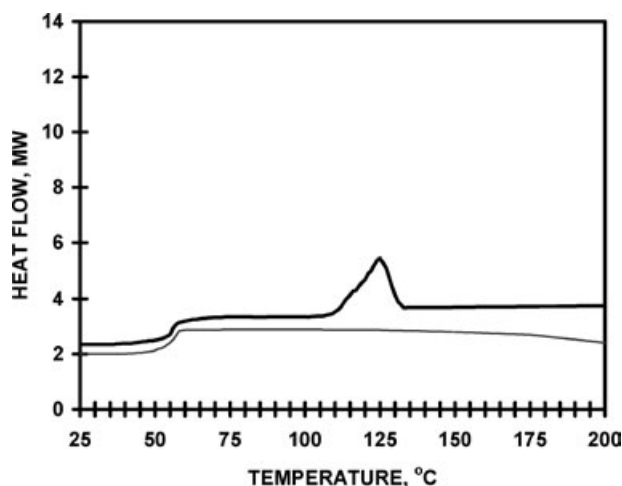

FIGURE 2. DSC of 80/20 (L-/D,L) PLA.

D,L concentration is 15%, or lower, is the polymer able to crystallize by thermal processing in a reasonable time frame. Consequently, the 85/15, 90/10, and 95/05 copolymers have greater practical potential than either the pure L- or 80/20 copolymer materials for film or molded products. The (100% L-)PLA was developed originally to be used in fiber form where the high degree of crystallinity and orientation would provide excellent strength.

The rate and extent of crystallization depends not only on the L- concentration. It also depends on molecular weight,[16] the presence or absence of nucleating agents,[15] and the time-at-temperature above T_g.[15] Figure 3 shows a DSC curve for a 90/10 copolymer sample quenched rapidly during

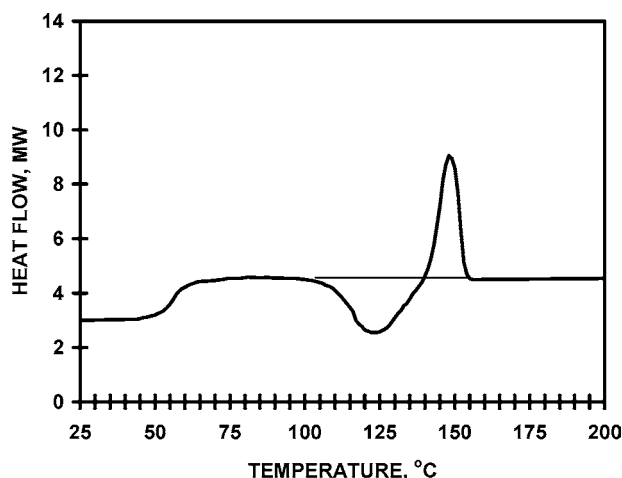**FIGURE 1.** DSC of 100% (L-) PLA.

FIGURE 3. DSC of 90/10 (L-/D,L) PLA.

injection molding. Note the crystallization exotherm between the glass transition temperature and melting temperature. Crystallization upon heating above T_g is seen even more dramatically in Fig. 4. This figure is a plot of the real component of the complex modulus versus temperature. It shows a sharp drop in the modulus at temperatures just above the T_g. This is the classic response of an amorphous polymer. At 10°C above T_g the modulus stops dropping, reaches a minimum at approximately 75°C, and then begins to increase until the temperature reaches 140°C. This increase in modulus above 60°C is due to crystallization of the polymer. Similar behavior was shown by Migliaresi and co-workers.[16] Figure 5 shows the modulus of the crystallized polymer over the same range of temperatures. Note the plateau region between the glass transition temperature and the melting point. Similarly, the DSC curve, Fig. 6, for the crystallized polymer does not show a melting exotherm in this region. The crystallized polymer has practical utility at temperatures up to 140°C. This upper limit is comparable to that of most commodity polymers.

Crystallization of the amorphous, but thermally crystallizable, copolymers by annealing could be initiated at temperatures between 75°C and the melting point. Annealing crystallizable PLA copolymers to induce crystallinity often produced two melting peaks. For example, Fig. 7 shows the DSC response of a 3 mm thick 90/10 copolymer sample that had been annealed for 5 min at 110°C. Note the lack of an exotherm in the plateau region, and the two distinct melting peaks at 145°C and 150°C. Annealing samples of this thickness beyond 5 min produced no observable increase in the degree of crystallinity
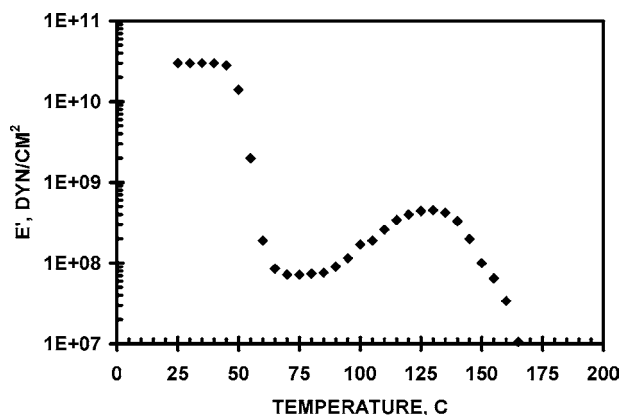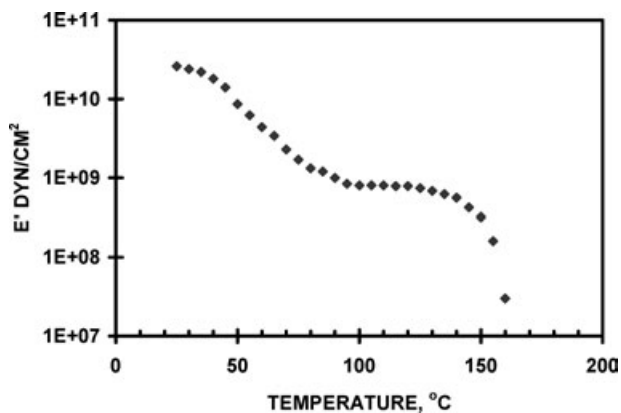

FIGURE 5. Dynamic modulus versus temperature for 90/10 copolymer after annealing for 2 min at 130°C.

achieved. Annealing for 1 min or less did not allow a 3 mm thick sample enough time to heat up to the temperature range required for annealing. When the 90/10 copolymer was annealed for long durations (up to 24 h), the lower melting endotherm merged with the higher melting endotherm. Interestingly, annealing at a higher temperature, 135°C, for 5 min did not produce complete crystallization. This is shown in Fig. 8. Annealing at temperatures close to the melting point produced only those crystals with the highest melting point. Longer annealing times were required to produce the more perfect higher melting crystals. This is, no doubt, a result of first melting the less perfect, lower melting crystals, and then reforming them into higher melting, more perfect crystals. This change in crystallization process from rapidly forming lower melting crystals to more
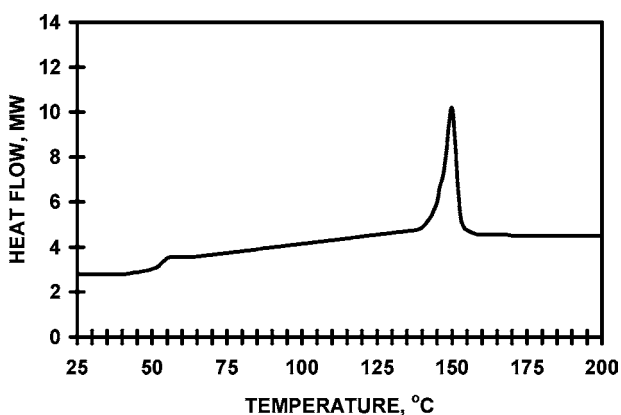

FIGURE 4. Dynamic modulus versus temperature for 90/10 copolymer as quenched from the melt.

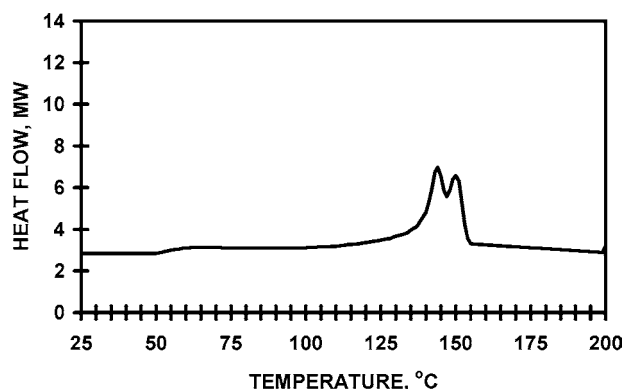**FIGURE 6.** DSC of 90/10 (L-/D,L) PLA annealed at 135°C for 1 h.

FIGURE 7. DSC of 90/10 (L-/D,L) PLA annealed at 100°C for 5 min.

slowly reforming higher melting crystals occurred gradually as the annealing temperature progressed from 100°C to 140°C.

The rate of crystallization also depended on the molecular weight of the polymer. For example, a very high molecular weight polymer, $M_w \geq 400,000$, inhibited crystallization. This was demonstrated by heating a sample that had been crystallized from solution during the polymerization process. The sample was heated above its melting point to destroy the crystallinity, and then reheated during the DSC run at 10°C/min. No evidence of either a crystallization endotherm at 150°C, or crystallization exotherm between 100°C and 140°C was observed. In many respects this is not important, since a PLA polymer with a weight average molecular weight ex-
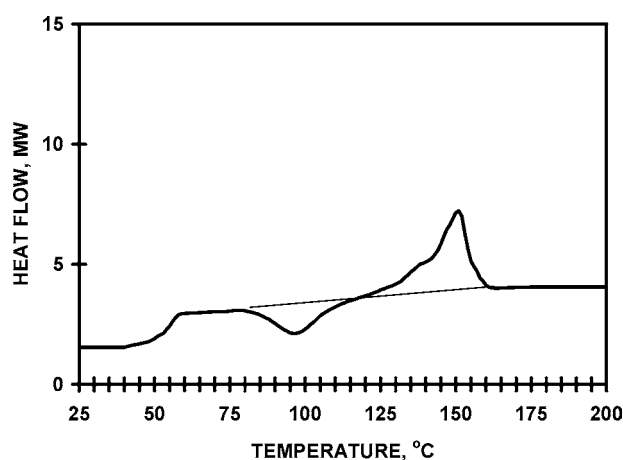

FIGURE 8. DSC of 90/10 (L-/D,L) PLA annealed at 135°C for 5 min.

ceeding 400,000 could not be injection molded, and was severely degraded during extrusion. The 90/10 copolymer, with a molecular weight consistent with the ability to crystallize ($M_w < 300,000$), develops crystallinity in the range of 30%, which is comparable to that achieved with PET.

Since annealing is not always the most desirable route to producing a crystalline polymer, nucleation was investigated. Annealing times on the order of minutes are not practical for most molded parts. The 90/10 and 95/05 copolymers were nucleated to increase their rates of crystallization. The addition of 1% calcium lactate increased the rate of crystallization of the 90/10 copolymer to the point where no crystallization exotherm was observed during heat up of a polymer sample that had been quenched from the melt during injection molding. Again, even the nucleated polymer could be quenched rapidly enough to inhibit crystal formation.

Effect of Crystallinity on the Rate of Degradation

Amorphous PLA has a glass transition temperature that is too low for many applications. In those cases, the crystalline form of the polymer is required to increase its upper temperature utility. Crystallinity can be induced in PLA, but often requires annealing, the use of nucleating agents, or induction by strain. While these procedures are appropriate and widely used in film and fiber processing, they are not always amenable to injection-molded parts.

Dried, nonend-capped 90/10 (L-)/(D,L) copolymer, having a M_w of 166,000, was extruded into 1.5 mm thick films at 190°C. After forming, the films were rapidly quenched to suppress crystallinity. One set of these amorphous films was biaxially oriented on an E. M. Long machine at 85°C to a draw ratio of 3× by 3×, and then heat set under tension at 110°C. These films were optically clear and were determined by DSC analysis to be about 33% crystalline. Both the oriented and unoriented films were aged at 32°C and 90% RH, and analyzed for molecular weight changes after 53 days. The molecular weight of the amorphous film dropped to 20,000 in this time period. The molecular weight of the biaxially oriented, semicrystalline film dropped to 56,000 in the same time period, despite the sample being 1/9 as thick as the amorphous film. Clearly crystallinity retards the rate of degradation.

Effect of End Capping on the Rate of Degradation

The base polymer investigated in this study was also a random copolymer of 90% (L-) lactide and 10% (L,D) racemic lactide. Twenty gram of the copolymer was dissolved in 200 mL of dry tetrahydrofuran, along with 2 mL of pyridine and 4 mL of acetic anhydride. End capping of acetic anhydride onto the hydroxyl end groups proceeded by refluxing the solution for 16 h. End capping was confirmed by NMR analysis. The polymer was recovered by precipitation in 1 L of methanol, followed by drying for 16 h under vacuum at 30°C. A control sample was put through the same procedure without the acetic anhydride added to the solution. Films were formed and aged at 32°C and 95% RH for 28 days. The copolymers were also analyzed by TGA to determine the rate of weight loss at 180°C.

End capping of the carboxyl end groups was accomplished in the same manner, with diazomethane substituted for the acetic anhydride. Finally, both end groups were capped with acetic anhydride and diazomethane. The results of the aging studies and TGA results are presented in Table II. Clearly, the presence of the end caps reduced the rate of degradation. The end-capped polymers degraded at less than half the rate of the uncapped polymer.

Effect of Plasticization on the Rate of Degradation

Amorphous PLA is quite brittle unless plasticized, a factor that further serves to reduce the upper temperature utility of PLA. When elevated temperature stability is not a requirement, or the polymer is used in its crystalline form, plasticization serves to make the resulting films, fibers, and coatings less brittle, and more impact resistant during use, yet able to degrade more rapidly when discarded. A very common and convenient plasticizer for PLA is the lactide monomer. Table III shows the effect of 10% lactide as a plasticizer in a film sample aged in seawater at Daytona Beach, FL. The water temperature ranged from 20°C to 29°C during the exposure period. While the unplasticized polymer also has a higher molecular weight to retard its degradation, that effect was not as great as the effect of plasticization.

Melt Processing Considerations

THERMAL DEGRADATION

The issue of the ideal molecular weight for PLA polymers for various applications has a number of factors to take under consideration. Ideally, injection-molded polymers should have a molecular weight that produces a viscosity in the range of 100 Pa-s to 10,000 Pa-s. These values are desired ranges and can be affected by shear sensitivity and other factors. Extruded and thermoformed products can be produced from polymers having higher viscosities and higher molecular weights.

The choice of molecular weight to achieve a desired viscosity is not open ended, however. A characteristic of PLA polymers is that they quickly lose their limited thermal stability when heated above the melting point. Table IV shows that even at 160°C, just 10°C above T_m, a significant level of molecular degradation will occur if the polymer is held at temperature for a sustained period of time. Migliaresi and co-workers showed that thermal degradation was due to chain splitting and not hydrolysis.[16] They observed molecular weight drops of over 50%, and concluded that large molecular weight reductions were unavoidable. Jamshidi and co-workers showed that oxidation did not occur to a measurable extent during thermal degradation.[17] They did show that molecular weight deterioration could be slowed by

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TABLE II

Effect of End Capping on Degradation Rate of 90/10 PLA Copolymer—28 Days at 32°C, 95% RH

	No End Caps	Hydroxyl Group End Caps Only	Carboxyl Group End Caps Only	Both Groups End Capped
Weight loss (%/min)	0.008	0.003	0.002	0.003
Physical condition of film	Cloudy, brittle	No change	No change	No change

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TABLE III
Degradation of 90/10 (L-)/(D,L) PLA Copolymer in Seawater −25°C, Salinity 35.9

	Plasticized Film		Unplasticized Film	
	Elastic Modulus (GPa)	Tensile Strength (MPa)	Elastic Modulus (GPa)	Tensile Strength (MPa)
Initial Properties	1.89	42.1	2.10	52.7
Exposure Time (weeks)	Relative Modulus (% Retained)	Relative Strength (% Retained)	Relative Modulus (% Retained)	Relative Strength (% Retained)
0	100.0	100.0	100.0	100.0
3	106.1	111.3	103.3	92.8
6	89.6	63.1	104.0	95.6
9	40.4	23.6	74.7	81.1

removal of the catalyst and end capping the chains. Otherwise, the drop in molecular weight must be anticipated and taken into account when defining primary processing conditions, annealing conditions, and expected property performance.

Thermal degradation considerations established a maximum processing temperature of 200°C. This upper processing temperature results in a very narrow processing window, approximately 12°C, for 100% (L)-PLA. The 90/10 copolymer has a broader processing window (40°C), by virtue of its lower melting point. This processing window is comparable to that of PET, which is also thermally sensitive. Finally, the molecular weight needed to be controlled such that the viscosity was appropriate for processing within this window. In PET, the molecular weight is often relatively low, compared with that of most other commercial polymers. Only recently have stabilizing agents been developed to enable higher molecular weight grades of PET to be processed without degradation. As mentioned previously, Jamshidi and co-workers showed that end capping PLA would significantly improve its thermal stability.[17]

TABLE IV
Effect of Temperature on the Molecular Weight of 90/10 PLA Copolymer

Initial MW	MW After 30 min at 160°C	MW After 30 min at 190°C
151,000 (Mn)	102,000	84,000
285,000 (Mw)	204,000	142,000
470,000 (Mn)	354,000	228,000
950,000 (Mw)	650,000	390,000

COLOR FORMATION

Unfortunately, the degradation process is complicated by the action of more than just molecular weight deterioration. Another process limiting phenomena associated with the upper limit of thermal processing is the development of color in the natural polymer when processed above 200°C. An interesting development associated with this phenomena was a result of the persistent presence of unreacted lactide in the synthesized polymer. The presence of unreacted monomer in the polymer had two effects. The first was to lower the glass transition temperature, classical plasticization. The second effect was to allow polymer chains that were broken during thermal processing to heal themselves without the formation of color inducing carbonyl groups. This has been demonstrated in the following experiment. All of the residual monomer was removed from a batch of the 90/10 copolymer. In one cut from this batch, 5% residual monomer was added back into the polymer via a feed port on a Baker–Perkins 30 mm co-rotating twin screw extruder. The melt temperature of the extrudate was 200°C. The extrudate had a distinct yellow color, and the weight average molecular weight of the polymer dropped from 513,000 to 322,000.

In a second trial the lactide monomer was added to constitute 15% of the polymer. Using the same processing conditions the extrudate's color was water white. GPC analysis, using THF as the solvent, showed little change in molecular weight during processing. The M_w of the polymer fed to the extruder was 307,000. The extrudate had an M_w of 324,000. One explanation that can be inferred from these results that the residual monomer repaired broken chains and lengthened other chains, instead

of permitting thermally induced molecular weight breakdown to occur. Another explanation that has been offered is that the residual monomer reduced the melt viscosity, thus reducing the viscous shear degradation that the polymer would normally have undergone.

The observation of healing of a specific degradation reaction is consistent with one of the many thermal degradation mechanisms offered by Jamshidi and co-workers.[17] They suggested that intermolecular transesterification to monomer and oligomeric esters can occur. The presence of a significant level of residual monomer can act to push the reversible monomer $\Leftrightarrow$ polymer reaction back toward the polymer side. Strong evidence for this was shown by the increase in thermal stability that occurred when the polymer was purified and the catalyst removed. Since the residual monomer is undesirable in most applications, it was removed from extruded films and fibers by vacuum evaporation during processing.

While preventing color formation during molding of PLA parts is not directly related to degradation control of those parts afterwards, the techniques used to prevent unwanted color do affect the degradation rate of the polymer. Preventing color in PLA films, fiber, coatings, or parts is a major consideration associated with the commercial development of the polymer. Under ordinary circumstances non-end-capped PLA, with a low concentration of residual monomer, will develop a yellow color during melt processing at temperatures above 190°C. Since the polymer cannot be efficiently pumped through an extruder below that temperature, color formation can be persistent. Molecular weight analysis has shown that the polymer will break down during melt processing unless stabilized.[18] Consequently, stabilization is critical if color formation is to be prevented.

RHEOLOGICAL CONSIDERATIONS

Rheological measurements and dynamic mechanical analysis (DMA) were done on a rheometrics mechanical spectrometer model 605. The testing frequency used for DMA analysis was 6.28 rad/s (1 Hz). Rheological measurements were made under an oscillatory strain of 10%. Mechanical properties were measured on an Instron testing machine at an extension rate of 2.54 cm/min. The viscosity–molecular weight relationship was studied extensively in a variety of ways. Figure 9 shows a plot of viscosity, at 1 rad/s, as a function of the weight average molecu-
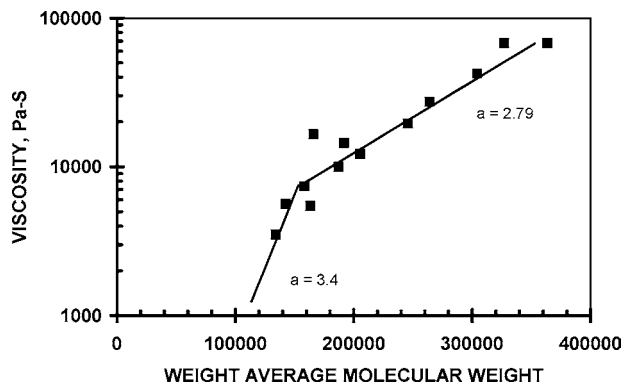

FIGURE 9. Viscosity at 1 rad/s versus molecular weight.

lar weight for a series of 90/10 copolymers. On this figure the viscosity was measured at 160°C to minimize molecular weight degradation during the investigation. Using the relationship

$$\eta = K M_{\mathrm{w}}{}^{a}$$

the data in Fig. 9 were divided into two regions. The relationship between the zero shear viscosity, η_0, and M_{w} has an exponent, a, of 3.4. The line drawn through the points with the lowest molecular weights has a slope of 3.4. The value of a for the remainder of the points is 2.79. This is most likely a result of not achieving the zero shear Newtonian viscosity at 6.28 rad/s in the oscillatory rheometer. The data presented in Fig. 10 show that higher molecular weights lead to greater non-Newtonian behavior. Note that the higher molecular weight polymer exhibits greater shear rate sensitivity than the almost Newtonian behavior of the lower molecular weight polymer.
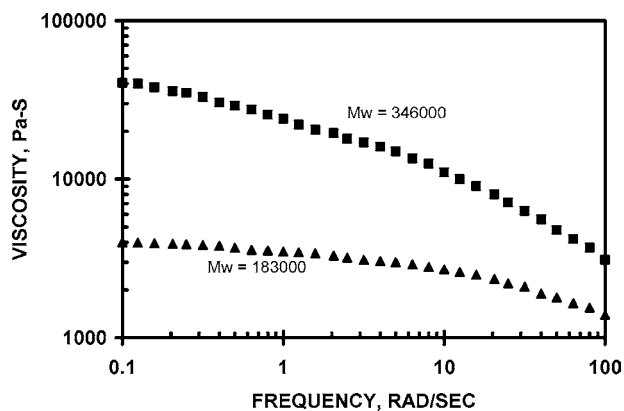

FIGURE 10. Viscosity versus shear rate for high and low molecular weight 90/10 PLA copolymer.
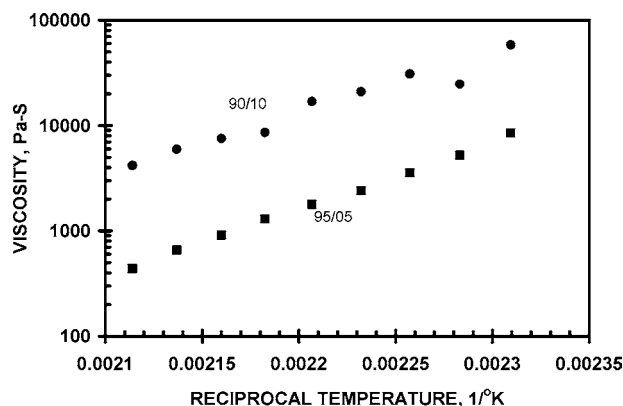
FIGURE 11. Viscosity at 1 rad/s versus reciprocal temperature.

Figure 11 shows the viscosity, at 1 rad/s, as a function of reciprocal temperature for a 90/10 and 95/05 copolymer. The slope, which represents the flow activation energy, is the same for both copolymers. The curves are displaced because the weight average molecular weight of the 90/10 copolymer (562,000) is more than twice that of the 95/05 copolymer (260,000).

Mechanical Properties

Tables V and VI contain the mechanical properties of a range of PLA polymers according to copolymer type and processing conditions. It should be pointed out that the samples tested include materials having a range of molecular weights, hence the data have primary value for comparative trends. The various processing conditions of the samples presented in Table V included simple injection molding, and injection molding followed by annealing for 5 minutes at 130°C. The samples presented in Table VI were extruded 1.5 mm thick films that were 3× by 3× biaxially orientated at 85°C. Half of the extruded and

biaxially oriented films were heat set under tension at 110°C for 10 min. In the latter case sufficient tension was applied to prevent dimensional changes during the heat setting process.

Table V shows that the 100% PLA polymer, when crystallized, has higher mechanical properties than the copolymers. This is as expected, as the (D,L) copolymer interferes with crystallization. The 100% PLA polymer also had a much higher molecular weight, a factor that also added to its high mechanical properties. Crystallization of the 90/10 copolymer provided small increases in tensile strength, modulus, and elongation-to-break. The lowest tensile strength was obtained from the amorphous 80/20 copolymer. Because of its higher molecular weight, the 80/20 copolymer did have a significantly higher tensile modulus and a slightly higher elongation-at-break than the 90/10 copolymer.

As Table VI shows, biaxial orientation increased the tensile strength, modulus, and elongation-to-break for all comparable polymers. Interestingly, the 80/20 copolymer showed the greatest increase in properties. This is somewhat surprising, since amorphous polymers usually do not show such large improvements in properties during orientation. DSC analysis of the oriented 80/20 copolymer, Fig. 2, showed that the polymer underwent strain-induced crystallization. It is well known that strain-induced crystallization is several orders of magnitude faster than thermal crystallization.[19] DSC analysis also showed that the 90/10 and 95/05 copolymers underwent strain-induced crystallization during the orientation process at 85°C.

Since these polymers have a T_g of only 56°C, the oriented film will shrink if heated to this temperature unless it has been heat set. As mentioned, heat setting was done by restraining the oriented film at 110°C for 10 min. The effect of heat setting time was not investigated. Heat setting resulted in a moderate reduction in strength and modulus as the process-oriented amorphous portion of the polymer relaxed into an unoriented condition. The mechanical properties of the heat set polymer were still higher than

TABLE V

Effect of Processing Conditions on the Mechanical Properties of Injection Molded PLA Copolymers

Copolymer Ratio	Morphology	σ (MPa)	E (GPa)	ε (%)	M_w
100/00	Crystallized	64.8	2.00	–	800,000
90/10	Crystallized	58.6	1.29	5.1	145,000
90/10	Amorphous	53.4	1.03	4.6	145,000
80/20	Amorphous	51.7	2.10	5.7	268,000

TABLE VI
Effect of Processing Conditions on the Mechanical Properties of Extruded and Biaxially Oriented PLA Copolymer Films

Copolymer Ratio	Secondary Process Conditioning	σ (MPa)	E (GPa)	ε (%)	M_w
95/05	None	68.6	1.88	56.7	120,000
95/05	Heat set at 110°C for 10 min	60.7	1.63	63.8	120,000
90/10	None	80.9	3.41	41.2	145,000
90/10	Heat set at 110°C for 10 min	70.1	2.76	20.7	145,000
80/20	None	84.1	2.94	18.2	268,000
80/20	Heat set at 110°C for 10 min	80.1	2.54	32.3	268,000

those of the molded or extruded material, and were considered good when compared to many commodity plastics. Of greater importance, however, was the thermal stabilization of the polymer film after undergoing the heat setting process. Heat set films could be thermoformed at 75°C to produce shapes that were dimensionally stable at temperatures up to 100°C. The amorphous 80/20 copolymer could not be thermoformed because its molecular weight was too high to provide satisfactory definition during part forming. The 95/05 copolymer could not be easily thermoformed because its low molecular weight resulted in tearing at corners and in sections of deep draw.

Variations in the data are due to the range of molecular weights of the individual samples, and differences in purity of the polymer obtained from the pilot plant polymerization runs. While all of the materials were above the critical molecular weight where the mechanical properties become independent of molecular weight,[16] molecular weight can still effect the properties through its effect on processing.

Summary

Polylactic acid copolymers of L and D,L enantiomers have a number of interesting and useful features. They can be formulated to provide a good balance between the crystallinity needed for a useful upper use temperature and that need to produce a "tough" plastic material. The major consideration that needs to be taken into account is the finite crystallization time. Even when nucleated, PLA copolymers can be quenched into the amorphous state. It would have been appropriate to conduct studies on the rate of crystallization at various molecular weights and under various thermal regimes

and nucleation conditions. Unfortunately, the pilot reactor used to produce the polymer did not have the requisite control to produce targeted molecular weights. Molecular weight control was to a "high" or "very high" degree. The fact that the molecular weight of the polymers changed significantly during processing also made any nucleation studies a rather random exercise.

PLA copolymers have a wider temperature processing window than (100%L-)PLA, and process in a manner similar to PET. They can be quenched into an amorphous polymer, and then crystallized by annealing. PLA copolymers can be strain crystallized during biaxial, or uniaxial orientation. Such polymer products as film and fibers can then be heat set under tension to produce strong, tough materials having good upper temperature stability.

The data generated in this program demonstrate that the rate of degradation of PLA can be controlled by relatively simple and common means. Moreover, the techniques used are adaptable to the polymer in either crystalline or amorphous forms, and suitable for items made by extrusion or injection molding. Control of molecular weight is obvious. Higher molecular weight polymers require more breakdown reactions to reduce the polymer to a size that can be digested by microorganisms. Inducing crystallinity also slows down the degradation process. Because of the relatively slow rate of thermal crystallization, the state and degree of crystallinity can be controlled by nucleation, annealing, and induction by strain. The ultimate ability to develop crystallinity is controlled by the degree of copolymerization of the L- and D,L lactide isomers.

End capping not only stabilizes the polymer, but inhibits color formation during melt processing. Color formation can also be prevented by plasticizing PLA with at least 15% lactide monomer. Plasticization makes PLA less brittle and increases the rate of biodegradation.

The fact that PLA and its copolymer degrades into water and carbon dioxide has some positive benefits in certain packaging and medical applications.

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