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THE CASE FOR POLYLACTIC ACID AS A COMMODITY PACKAGING PLASTIC

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ABSTRACT

Poly lactide, sometimes called polylactic acid (PLA), meets many requirements as a packaging thermoplastic and is suggested as a commodity resin for general packaging applications. Its general physical properties and melt processing ease are similar to conventional packaging resins. PLA slowly degrades by hydrolysis in even a slightly moist environment over a period of several months to a year to environmentally-friendly products, which, in turn, biodegrade to carbon dioxide, methane, and water. PLA is a clear, colorless thermoplastic when quenched from the melt and is similar in many respects to polystyrene. When plasticized with its own monomers, PLA becomes increasingly flexible so that a continuous series of products can be prepared that can mimic PVC, LDPE, LLDPE, PP, and PS. Degradation is increased with increasing plasticizer, and shelf life is favored by decreasing plasticizer content and/or orientation. Orientation also substantially improves tensile strength, modulus, and heat stability. A general rationale for the commercial development of PLA is presented.

INTRODUCTION

The proposition of introducing PLA as a commodity thermoplastic when presently it is an expensive, niche, biomedical material is an ambitious goal. When I first advanced this proposition many years ago, it was based on some experience with the properties of PLA and what I thought was an excellent to good manufac-

turing and cost potential, desirable packaging properties, good processability, and belief in a need for biodegradable plastics. Over the years the ideas were focused and refined, and eventually became patent applications. To date, no "Achilles heel" has been found to the basic proposition. The applications of PLA for both biomedical and nonbiomedical uses has been a consistent theme of our laboratories for many years [1-5], and recently our patents have begun to emerge on the use of PLA as an inexpensive, general utility, disposable packaging resin [6-10]. This paper is an attempt to summarize the latter.

PLA can be a well-behaved thermoplastic with a reasonable shelf life for most single use packaging applications, and when disposed of in the correct manner (or carelessly left as litter) will hydrolyze to harmless, natural products. It could be a technical and economic solution to the problem [11-14] of the eventual disposal of the very large amount of plastic packaging used in this country. In 1993 some 17.3 billion pounds of disposable plastic packaging was sold in the United States [15]. A small but significant percentage of this is disposed of as litter, which becomes a blot on the landscape and a threat to marine life. Mortality estimates are as high as 100,000 marine animals and 1 to 2 million sea birds per year [14]. PLA has a degradation time in the environment of the order of 6 months to 2 years, which compares to 500 to 1000 years for conventional plastics such as polystyrene (PS) and polyethylene (PE). We have examined PLA from the standpoint of physical properties, processing, and possible commodity production routes. An overview of this is presented below, along with some opinions on cost, competition, and market acceptance.

COMPOSITION AND FORMULATIONS

PLA is a polyester that can be prepared at a low molecular weight by the direct condensation of lactic acid as shown in Fig. 1. However, the condensation reaction is an equilibrium and does not readily proceed to a high molecular weight. A better route is through the intermediate monomer, lactide. The latter is customarily prepared from oligomeric PLA by a tedious cracking procedure, which is not easily scalable to volume quantities. The recent publication [10] of a practical method for commercial lactide production does much to make a case for commodity PLA. The new monomer route uses easily obtainable dimers and trimers of lactic acid in a process more amenable to chemical engineering. Referring to Fig. 1, it can be seen that the monomer and the polymer can have stereochemical variations, that is, there can be L-, D-, or meso-forms of the monomer units. The polymerization of pure L-lactide to L-PLA produces a material that is very high melting, has poor processing properties, and crazes easily because of its high crystallinity. The D,L-PLA is an amorphous polymer with a T_g of 60°C, which is too low for many packaging uses. A better composition for volume packaging resins is the 90/10 copolymer of L-/D,L-lactide. This material can be readily polymerized in the melt, can be oriented above its T_g , and is easily melt processible. The 90/10 comonomer mixture melt polymerizes with sufficiently low melt viscosity at 150 to 175°C to permit stirring during polymerization and practical discharge of the reactor if the molecular weight (M_w , by GPC) is below about 300,000.

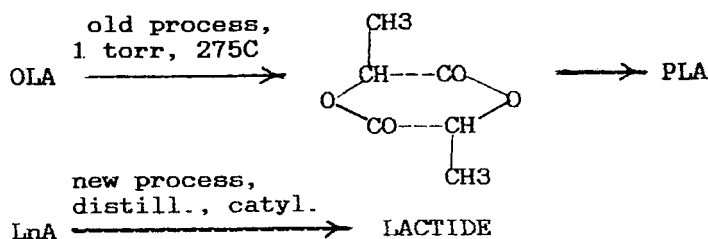
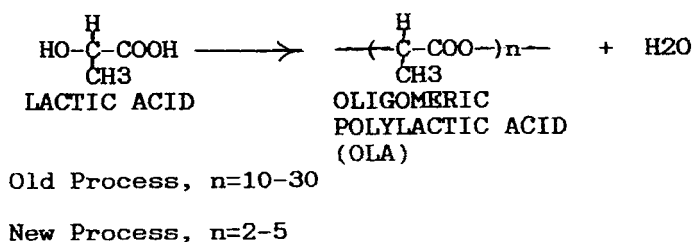


FIG. 1. Chemical reactions and intermediates in the production of PLA.

By way of contrast, L-PLA must be polymerized above 175°C to obtain a sufficiently low melt viscosity to permit discharge from the reactor.

PLA can be plasticized with lactide or oligomeric lactic acid (OLA, cf. Fig. 1) to prepare a continuum of products which vary from very stiff to tough to quite flexible, depending on the amount and type of plasticizer. These plasticizers regularly lower the T_g of the formulation with increasing amounts of plasticizer and impart very little odor or taste to the mixes since the mixtures are intimate dispersions of lactide and OLA in PLA [6, 10]. Films of these dispersions are clear and transparent. Their physical properties are discussed below.

COMMODITY PRODUCTION

Lactide can be polymerized to PLA using a catalyst such as a tin salt or ester as shown in Fig. 1. For commodity production this can be done in the melt with cost, safety, and toxicity advantages. The polymerization temperature should be maintained below about 185°C since PLA discolors rather quickly above this temperature, and this is not desirable for colorless, transparent packaging applications. The M_w (by GPC) should not exceed about 300,000 because then the melt viscosity of the PLA becomes so high that it is difficult to discharge a batch reactor. With partial conversion of monomer to polymer, the residual lactide acts as a plasticizer and lowers the working temperature and melt viscosity of the PLA. This also has advantages of shortening the cycle time of the polymerization. Subsequent processing of the PLA can include compounding with lactide so that a partial monomer-to-polymer conversion can be desirable. Alternatively, lactide can be removed in the

compounder at a late stage devolatilizer. One basic PLA plant with both polymerization and compounding sections could, in principle, prepare base stocks of PLA resins in various molecular weights and formulate them many ways to meet the many requirements of conventional resin types and grades. Note that all the chemicals, except catalyst, are lactic acid derived, as shown in Fig. 1.

PHYSICAL PROPERTIES

At high monomer-to-polymer conversion, and when properly prepared as discussed above, PLA is colorless, transparent, and quite stiff, which is reminiscent of polystyrene (PS). This combination of properties is rare for a volume thermoplastic resin. Because of its stiffness, PS films are self-supporting. PLA that is unplasticized is also very stiff with tensile properties similar to PS. Table 1 [6, 7] lists some comparisons. The previously mentioned 90/10 copolymer of L-/D,L-lactide is preferred because of property and processing advantages. Amorphous, 90/10, L-/

TABLE 1. Some Basic Physical Property Comparisons of PLA and Polystyrene

Physical property	PLA ^a		PS ^b	
	Oriented	Unoriented	Oriented	Unoriented
Ultimate tensile strength: ^c				
psi	14,700	6,900	7,400	7,015
MPa	101	48	51	48
Elastic modulus:				
psi	564,000	221,000	450,000	240,000
MPa	3,889	1,524	3,103	1,655
Elongation, %	15.4	5.8	4.0	—
Impact strength, notched				
Izod:				
ft-lb/in	—	0.44	0.4	0.24
mN/m	—	23	21	13
Deflection temperature				
under load:				
°F	181	127	200	—
°C	83 ^d	53	93 ^e	—
Specific gravity	1.25	1.25	1.05	1.05
Melt flow rate:				
200°C	—	46	—	3.5
155°C	—	2	—	—

^aL-/D,L-Lactide copolymer.

^bCrystal polystyrene, Amoco R3.

^cASTM D882.

^dAnnealing temperature.

^e264 psi (1.82 MPa).

D,L-lactide copolymer has a tensile strength of approximately 6800 psi (47 MPa) when the residual lactide is 5%, and 8000 psi (55 MPa) at 0 to 2% lactide. These values agree with that of Vert [16], who found a tensile strength of 6670 psi (46 MPa) for the 75/25 copolymer of L-/D,L-lactide. Vert also noted that residual monomer has an influence on strength and other properties. However, it should be noted that it makes a great deal of difference whether the monomer is intimately dispersed or phase separated [6, 7]. In the former case the monomer acts as plasticizer. With a modest orientation of 3-5X, the values of tensile strength and moduli approximately double [17]. The increased L-content also has advantages in better strength as shown in Fig. 2, which Vert [16] also noted. Pennings also has reported on the physical properties of PLA with respect to their biomedical applications [20]; however, the listed value of 54.4°C for the T_g of the L-/D,L-copolymer indicates the presence of about 4% plasticizing monomer [17]. The use of crystallinity effects are useful with PLA [16-19, 21]. In addition to orientation, spherulitic crystallinity can be used to improve the tensile strength and hydrolytic stability of PLA although there can be a loss of extensibility. At very high crystallinities, such as those seen in PLAs with 98 to 100% L-forms, fabrication can be difficult because of crazing. Where optical transparency, strength, and higher extensibility are all needed, then orientation is desirable. The 90 to 95% L-copolymer (10 to 5% D,L) is easily quenched from the melt to transparent materials and did not show subsequent evidence of spherulitic crystallization for the lifetime of the fabricated PLA specimens.

Flexible PLA formulations utilize the monomer, lactide, as plasticizer. Whereas the residual monomer in PS must be removed down to the ppm level because of toxicity reasons, the residual lactide in PLA hydrolyzes to lactic acid, a substance occurring naturally in the body and in food. Lactide has a number of other advantages. Its incorporation as a plasticizer during polymerization allows

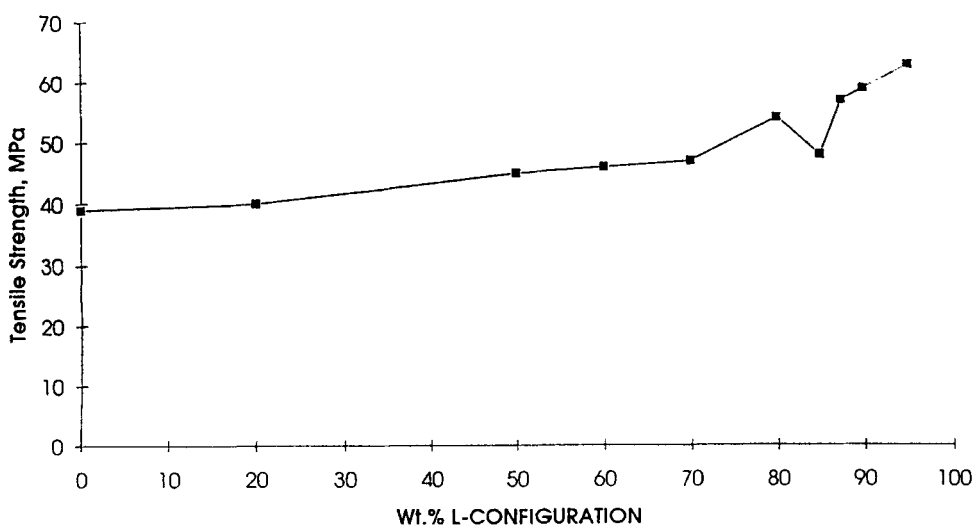


FIG. 2. Effect of configuration on tensile strength.

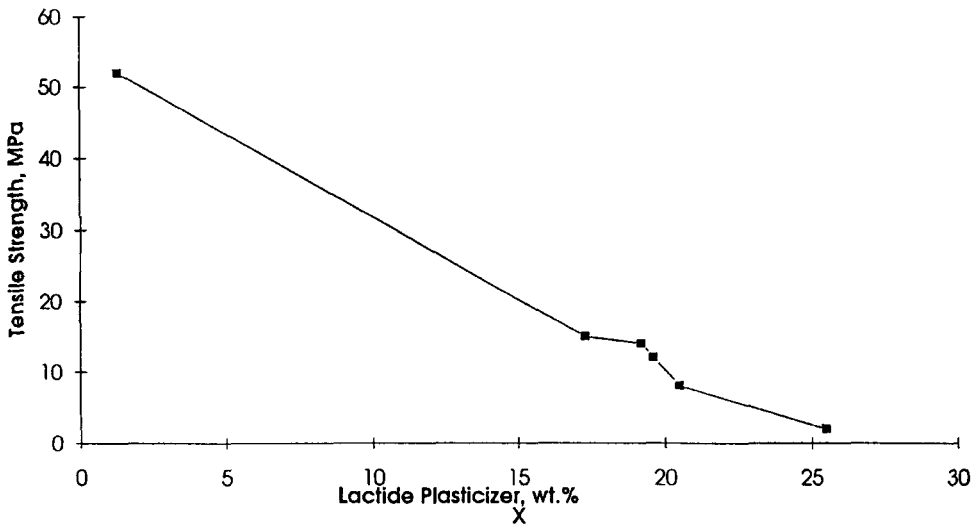


FIG. 3. Plasticizer effects on strength.

shorter cycle times in the polymerization reactor. Thereafter, lactide lowers the melt viscosity during reactor handling and during compounding, thereby easing melt processing and preventing discoloration as well as maintaining molecular weights. The plasticization of PLA provides a systematic attenuation of properties and a broad range of compounds for various applications. Some data are shown in Figs. 3 and 4. The basic tensile physical properties of a PLA and a PE are compared in Table 2 [7]. Both materials can be fine tuned over a range of values for specific package applications. The data of Table 3 [7] illustrate the broad range of proper-

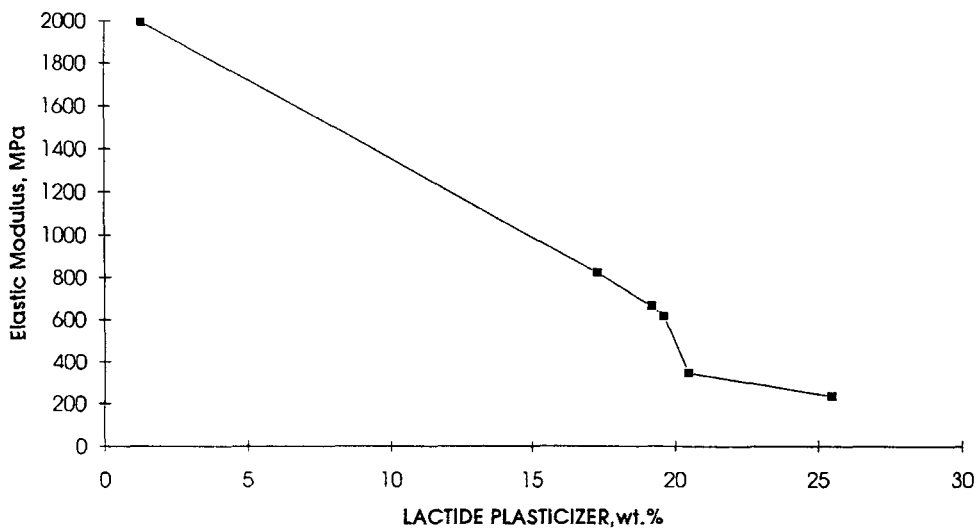


FIG. 4. Effect of plasticizer on modulus.

TABLE 2. Comparison of Polyethylene to PLA

Property	LDPE	PLA ^a
Tensile strength:		
kpsi	2.18	3.19
MPa	15	22
Elongation, %	261	280
Tangent modulus:		
kpsi	54.9	36.6
MPa	379	252
100% Modulus:		
kpsi	1.77	0.74
MPa	12	5
200% Modulus:		
kpsi	1.82	1.2
MPa	13	8
HDT:		
264 psi, °F	95	122
1.82 Mpa, °C	35	50

^aLactide plasticizer equals 19.5 wt%.

ties that can be obtained, and some similarities to conventional thermoplastics can be noted.

Another useful PLA plasticizer is OLA, which can come from the polymerization plant (cf. Fig. 1). PLA and OLA also can be intimately melt blended to transparent materials. The property modifications are illustrated by the data of Figs. 5 and 6 [7]. A substantial amount of OLA can be compounded into PLA with significant savings on the cost of production of the final compounds. In practice, both lactide and OLA can be used in combination as plasticizers to meet product demands since various combinations offer different advantages in strength, moduli, elongation to break, shelf life, and cost. One advantage of OLA is its use as a high temperature plasticizer. Lactide, alone as a plasticizer, will volatilize readily if attempts are made to add it to an open melt of unplasticized PLA. By adding OLA first to the melt, the melt temperature can be dropped before adding the lactide.

TABLE 3. Physical Properties of PLAs with Different Amounts of Plasticizer

Lactide plasticizer, wt%	Elastic modulus		Yield strength		Break strength		Strain at break, %
	kpsi	MPa	psi	MPa	psi	MPa	
25.5	33.7	232	310	2	2440	16.8	546
19.2	95.5	658	1970	14	4240	29.2	536
17.3	119	820	2230	15	2290	15.8	288
1.3	289	1993	—	—	7500	51.7	3

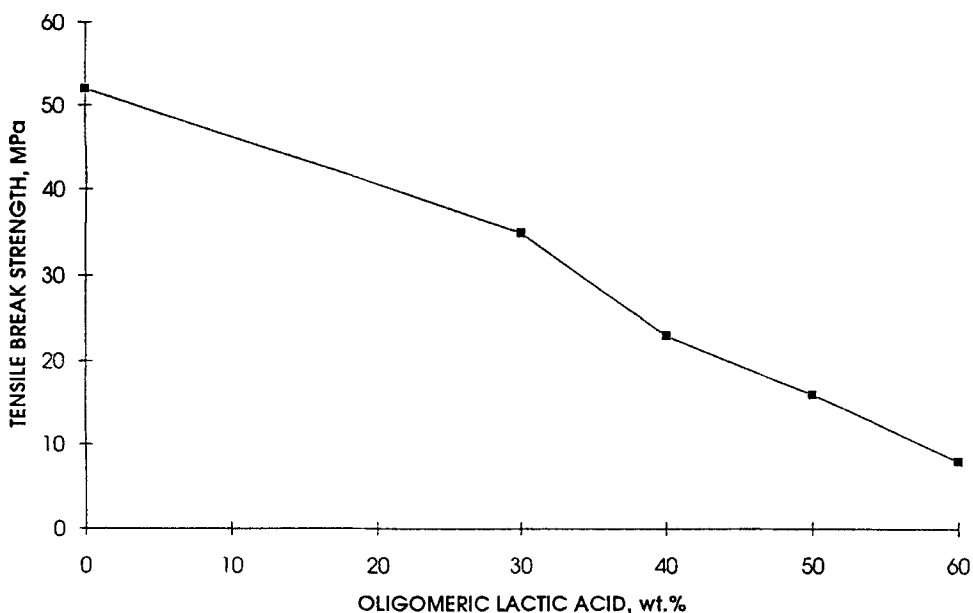


FIG. 5. Break strength of OLA-PLA blends.

With increasing OLA or lactide plasticizer, T_g s of the melt blends are lowered so that, for example, a well-plasticized PLA (15 to 20% lactide, or 30 to 40% OLA) can have a T_g of approximately 32 to 40°C, depending on the plasticizer amount and the intimacy of the dispersion. Figure 7 illustrates this. The films of these compounded PLAs are transparent, colorless, and have a faint to nonexistent odor and taste. The extractables in both hexane and alcohol-water are quite low, in the ppm range.

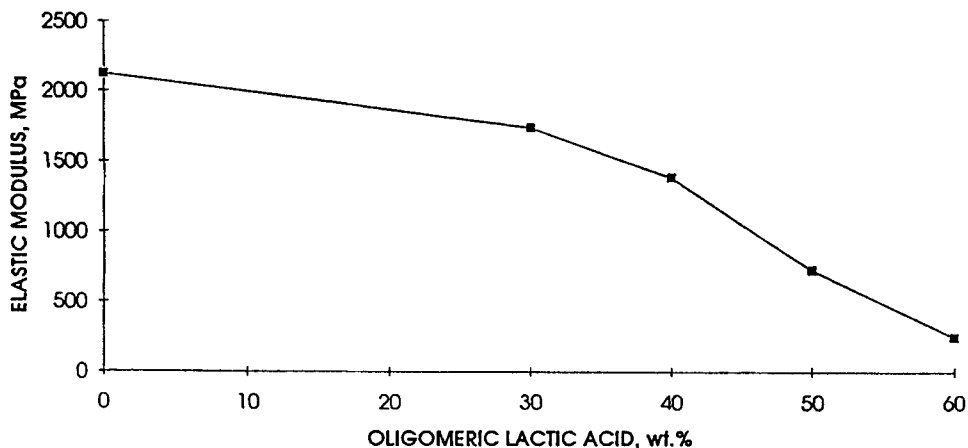


FIG. 6. Elastic moduli of OLA-PLA blends.

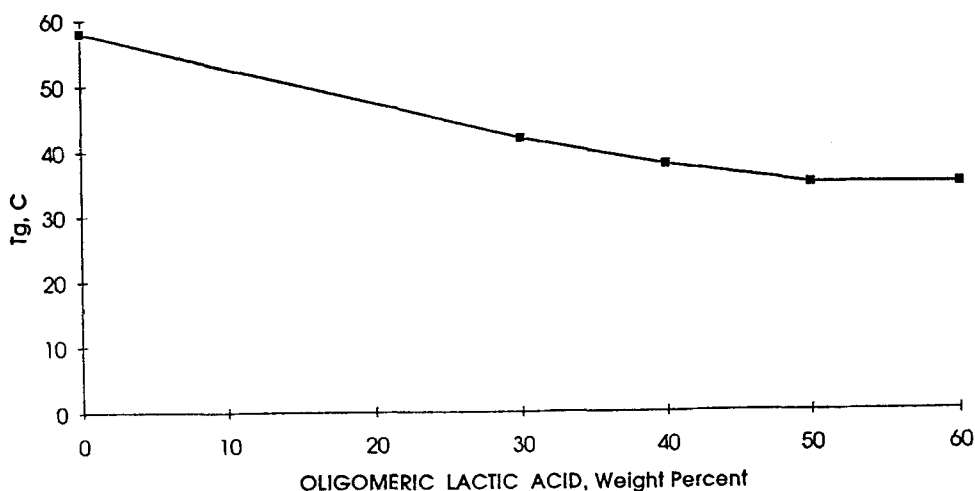


FIG. 7. Dependence of T_g on OLA content.

MELT PROCESSING

The polymerization of pure L-lactide to L-PLA produces a material that is very high melting, has poor processing properties, and crazes easily because of its high spherulitic crystallinity. L-PLA is difficult to keep transparent, even when quenched from the melt. D,L-PLA is an amorphous polymer with a T_g of 60°C, which is low for many packaging uses. A better composition for volume packaging resins is the previously mentioned 90/10 copolymer of L-/D,L-lactide, which is quite melt processible and quenches from the melt with transparency [17]. This copolymer also has a T_g of 60°C [6, 16], but it is easily orientable and heat set to provide a transparent and ordered composition that is form-stable at elevated temperatures. Thus, the inherent weakness of a low T_g is overcome. The melting point of the copolymer then becomes the limiting temperature for form stability. In practice, this temperature is set by the drawing and annealing temperatures, which are somewhat less than the polymer melting temperature.

Poly lactide melts are shear thinning, similar to polystyrene [17]. The melt viscosity vs shear rate curve of PLA at 155°C approximates that of PS at 200°C. This is illustrated in Fig. 8. The melt viscosities of high molecular weight PLA are 5,000 to 10,000 poise (500 to 1000 Pa·s) at 10 to 50 reciprocal seconds. The weight-average molecular weights (M_w) of these PLAs, as judged by GPC, are about 100,000 for injection molding to about 300,000 for cast extruded film grades. These molecular weights and the amount of plasticizer govern the usable melt viscosities required for melt processing in the polymer packaging industries. Although these M_w s are lower than those used in biomedical applications, they are a good compromise of processibility and end use properties. Some data in Table 3 are typically M_w s and basic properties for several grades of PLA packaging resin types. It was observed that PLAs have an upper limit of about 388°F (198°C), above

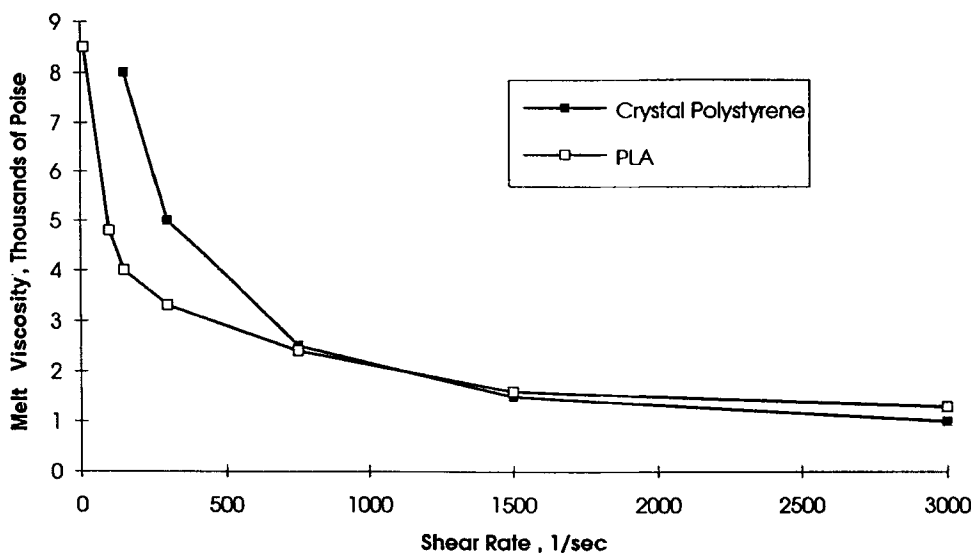


FIG. 8. Melt viscosity comparisons.

which they discolor rapidly. This working temperature is dependent on the melt viscosity, which is, in turn, dependent on the M_w s of the PLAs, the amount of plasticizer, the shear rate, i.e., the type of melt processing, and the amount of work put into the polymer. In addition to flowing through a compounder, extruder, or molding machine, etc., the PLA must exit a polymerizer as a melt. As it turns out, the upper M_w for discharge from a reactor and that for a compounder are about the same, approximately 200,000. Thus, for example, a PLA melt that is stirred or discharged from a reactor at 160 to 175°C has a zero shear viscosity of 100,000 poise (10,000 Pa·s). This will be somewhat lower at 1 to 10 reciprocal second shear rates, typical of stirred, bulk polymerizates. At film extrusion shear rates, e.g., 100 to 200 reciprocal seconds, the melt viscosity drops to about 4000 poise (400 Pa·s), which is also acceptable for this melt process.

PLA films can be oriented up to about an 8X draw before showing strain whitening. Considerable enhancement of properties are found at nominal draws of 3 to 5X. These remain transparent. Orientation of 5X produced tensile strengths of 13,000 to 16,000 psi (90 to 110 MPa) with elongations to break of approximately 20 to 30%. Tangent moduli were approximately 500,000 psi (3447 MPa). PLA resins also performed well in foaming and blown film studies, which will be reported by a separate communication. They can be impact modified [9] and melt blended with a wide variety of conventional packaging resins [8].

The PLAs must be protected from moisture during melt processing as do several conventional packaging thermoplastics, including PET. Otherwise, the PLAs are well-behaved thermoplastics that can be readily processed by conventional processes, including extrusion, injection molding, blown film, and foams.

DEGRADATION STUDIES

Films of PLA, both plasticized and unplasticized, were examined for changes upon standing during ambient conditions and exposures to seawater. Some changes in physical properties after seawater exposure are shown in Table 4. These tests were conducted at Battelle's Daytona Laboratory, outdoors in saline water, beginning during the spring (first 3 weeks at 5 to 21°C) and continuing into the summer when temperatures reached 27°C. The film specimens were prepared by compression molding. The unplasticized films showed changes in physical properties in approximately 12 weeks, the films plasticized with OLA in about 9 weeks, and those heavily plasticized with lactide showed almost immediate effects. A wide latitude of shelf lives and degradation times are possibly by the use of different amounts and types of plasticizers. Compression-molded films with little plasticizer will not show obvious changes for about 1 year when exposed to normal room air at 70°F (21°C) and 50% RH. OLA plasticized films are similar. Those heavily plasticized with lactide hydrolytically degrade much faster. The degradation of PLAs occurs by several overlapping steps. In the first step there is a diffusion-controlled invasion of moisture into the PLA. In the second step hydrolysis occurs to progressively lower the molecular weight. In the final step microorganisms digest low molecular weight hydrolysis products. This series of events requires a year or two for completion depending primarily on the temperatures, the moisture, and the residual lactide that is present in the PLA. The low lactide-containing PLAs show an obvious loss of strength and transparency in about 9 weeks of warm seawater exposure, or about 1 year in ambient air and humidity. Vert [16, 18] reported in more detail on the degradation of PLA.

TABLE 4. Tensile Properties after Seawater Exposure^a

Composition	Seawater exposure, weeks	Tensile properties, MPa			Strain at break, %
		Elastic modulus	1% Secant modulus	Break strength	
90/10 copolymer with 5% L-PLA	0	2103	2013	52	4.7
	3	2172	2075	49	3.1
	6	2186	2186	50	3
	9	1572	1586	43	3
	12	2448	2365	27	1
90/10 copolymer with 10% OLA	0	1896	1896	42	2
	3	2006	1937	47	2.9
	6	1696	1696	27	2
	9	1455	724	10	2
	12	710	710	12	1
92.5/7.5 copolymer with 20% lactide	1	(too brittle to test)			

^aFilms were compression molded, 12–17 mil.

Both PLA and OLA can be forcibly hydrolyzed in the monomer plant with boiling water, or in a steam autoclave, to obtain lactic acid solutions. This amounts to a "molecular recycling." It allows recycling of both manufacturing-plant materials and post-consumer packaging.

MARKET ACCEPTANCE AND COMPETITION

In 1985 the cost of lactic acid at the 200 million pound/year scale was estimated at about \$0.30/lb [5]. Recent trade press announcements of lactic acid polymers with estimates of selling prices of about \$1.00/lb are consistent with this estimate [11-13].

The estimated selling price of PLA is higher than that of conventional commodity polymers. Recall that PS has had 30 years of experience in coming to scale. The price of PS has varied from about 40 to 60 cents per pound since 1989 to the present. PLA could benefit also from stable renewable resource supplies, whereas conventional resins are dependent on a fluctuating supply of foreign crude oil.

Market acceptance would have to come from the growing green movement, at first into niche markets. The competition in these markets would be:

1. Polyhydroxybutyrate-valerate, which has an apparently much higher price, estimated at \$4 to \$10/lb [12].
2. Photodegradables, which require sunlight for disposal.
3. Recycling of conventional plastics, which obviously cannot serve all the plethora of the many plastic types, grades, formulations (molecular weights, fillers, dyes, pigments), blends, and multi-plyes.
4. Cellulose acetate (probably the diacetate), if a low price, biodegradable plasticizer can be commercially developed. Some possibilities for this could be lactide, OLA, and glycerine diacetate [22]. In general, it is difficult with the cellulosic and starch esters to find a composition that will simultaneously be thermoplastic, biodegradable, and economic.
5. Polycaprolactone and its copolymers could be competition if the quoted monomer price for caprolactone could be lowered by about one-half.

In comparison, PLA would have major advantages in cost and versatility, and could possibly play a significant role in ameliorating the plastics pollution problem.

CONCLUSIONS

If PLA is to compete in the commodity packaging market, it must be cost and technologically effective. With regard to the latter, PLA has excellent physical properties that mimic conventional thermoplastics, retains them through an adequate shelf and service life, and once disposed of will degrade in the environment to natural products. In addition, PLA melt processes well with similar rheology to conventional thermoplastics and has wide potential utility for the many types and specialized grades that now serve the disposable packaging industry. Our studies to date have not revealed any insurmountable objections for the use of PLA as a commodity resin. Battelle originally pioneered the concept of PLAs for nonbiomed-

ical applications [3]. Battelle has assigned its basic patents and intellectual property to Ecopol, LLC, of Golden, Colorado (formerly Biopak Technology, Ltd.), a partnership of Battelle Memorial Institute and ACX Technologies. A number of companies have announced pilot-plant studies of PLA processes.

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