



Modification of PLA with Mirel[®] a-PHA Copolymer

Mirel[®] a-PHA (polyhydroxyalkanoate) biopolymers are 100% bio-based and made from renewable plant sources. New technology developed by Metabolix enables the production of amorphous PHA (a-PHA), a rubbery polymer with a Tg of about -30°C and having no crystallinity. It is compostable under US ASTM D-6400 and EU EN-13432 standards and is also soil degradable (ASTM D-5988), marine degradable (D-7081), and degradable under both meso- and thermo-philic anaerobic conditions (D-5511).

Poly(lactic acid) (PLA) is a 100% bio-based material made from renewable plant sources. It is compostable according to the US and EU standards. It is characterized by excellent clarity, Tg of 60-65°C, and a high modulus of about 3 GPa.

Improvement of the toughness-modulus balance of PLA can be achieved through blends with Mirel a-PHA biopolymers. Masterbatches (MB) are a convenient method of incorporating a-PHA biopolymers by pellet blending for injection molding, sheet extrusion, cast and blown films, foam processing, fiber extrusion or any other melt process.

MBs are available with different PLA grades to match the rheology of different process requirements. Current MBs contain 45% a-PHA and 55% PLA.

Figure 1 shows the effect of a-PHA on reduction of the flexural modulus of PLA. The slope of the line is about -57 MPa/% a-PHA. Through pellet blends of PLA and MB, the desired level of modulus reduction can be achieved.

Figure 2 shows the toughening of PLA by a-PHA copolymer. Two different PLA polymers were used. Ingeo[™] 3052D is a standard injection molding grade with a melt index of of 14 g/10min (210C, 2.16 kg). Ingeo 3251D, with a melt index of 80, is a high flow grade for difficult to fill parts. In both cases, significant increases in toughness are observed. The higher molecular weight 3052D is easier to toughen so a required level of toughness can be achieved with lower levels of a-PHA. 3052D is the resin choice for injection molding unless high levels of flow are required.

It is important to minimize the time/temperature history during injection molding. While a-PHAs are significantly more thermally stable than classical semi-crystalline PHAs, minimizing the heat history will maintain high molecular weight and result in increased toughening efficiency. Residence times can be minimized by using a high ratio of barrel volume to shot size

Fig. 1 Effect of a-PHA on Flexural Modulus

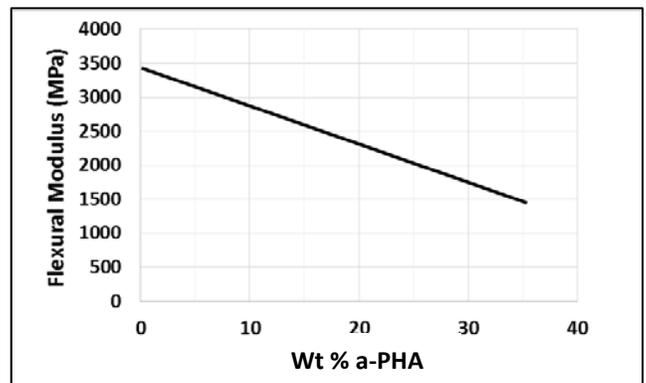
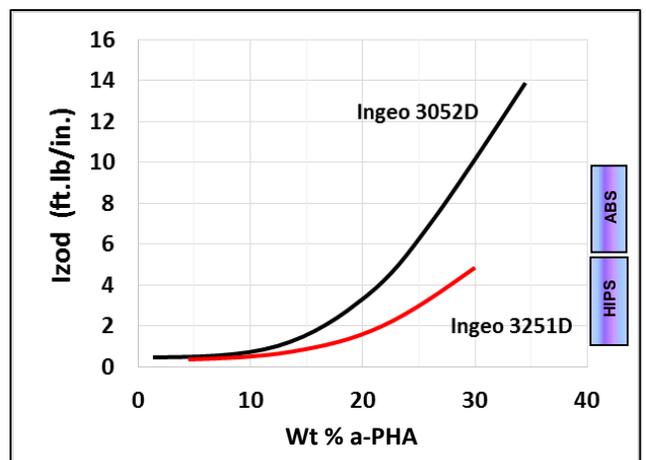


Fig. 2 Effect of a-PHA on Izod Impact Strength



Analogous to the reduction of Flexural Modulus shown above, Figure 3 shows the effect of a-PHA on tensile yield stress. The effect is similar independent of the grade of PLA.

Figure 4 shows the improvement in ductility that can be achieved as measured by tensile elongation. Again, the higher molecular weight PLA is more efficiently toughened.

To evaluate a-PHA in sheet extrusion, a masterbatch was made with extrusion grade Ingeo PLA4032D. Pellet blends with 4032D were extruded into 15 mil sheet.

Figure 5 shows the improvement in dart impact strength per ASTM D-1709. In high molecular weight sheet grade PLA4032D (RV=4.0, MI=3), effective toughening occurs at 5% loading of a-PHA. This can be compared to lower molecular weight PLA (compare to Figure 2).

Figure 6 shows the haze level of the extruded 15 mil sheet. In applications where the sheet will be thermoformed, haze will decrease rapidly as the sheet is thinned.

Fig. 3 Effect of a-PHA on Tensile Yield Stress

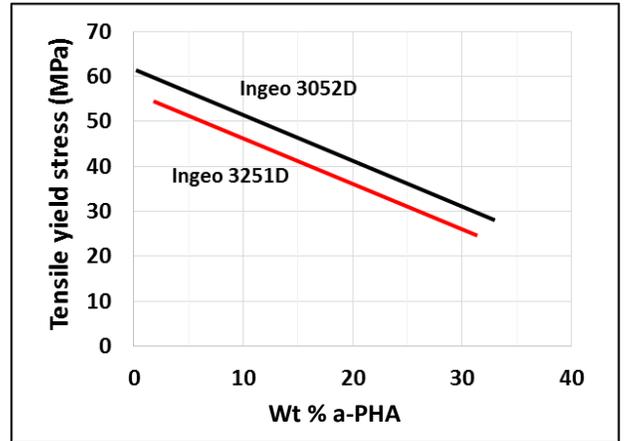


Fig. 4 Effect of a-PHA on Elongation at Break

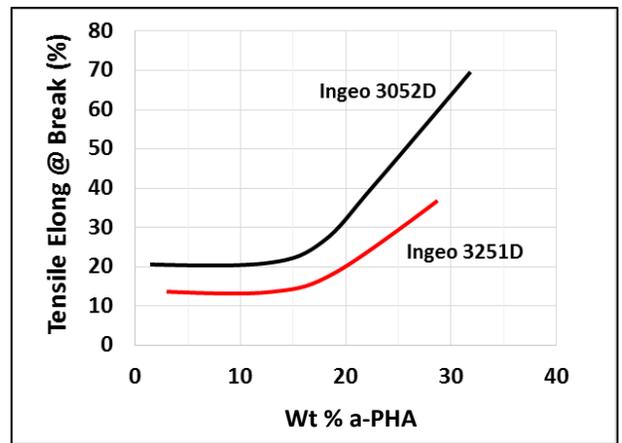


Fig. 5 Effect of a-PHA on Dart Impact Strength

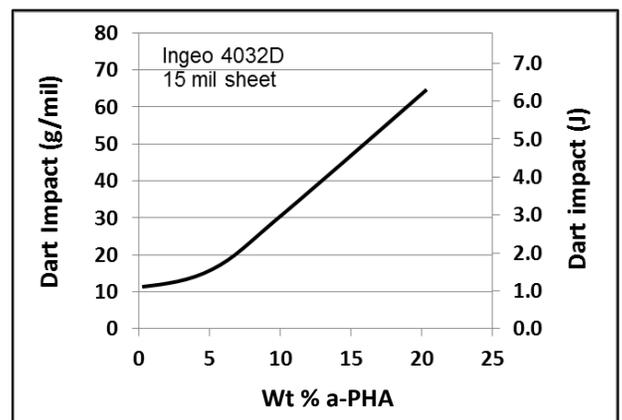
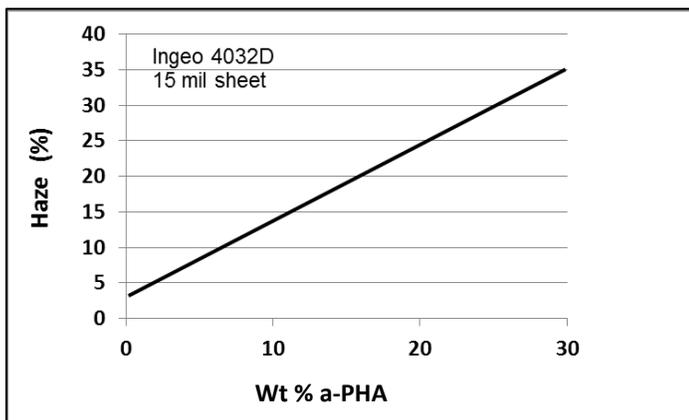


Fig. 6 Effect of a-PHA on Haze of extruded sheet



Sheet containing 0 and 5% PHA was impacted with a 752 gram (1.66 lb.) dart from a height of 66 cm (26 in.) as shown in Figure 7. While the PLA sheet shattered with many cracks, sheet containing 10% a-PHA has significantly improved impact strength.

The 15 mil sheet was rapidly cut on a shearing paper cutter. Figure 8 shows that the presence of 5% a-PHA dramatically improves the quality of the cut edge by eliminating sharp spurs and radial cracking.

Fig. 7 Dart impact on 15 mil sheet containing (a) 0 and (b) 10% a-PHA

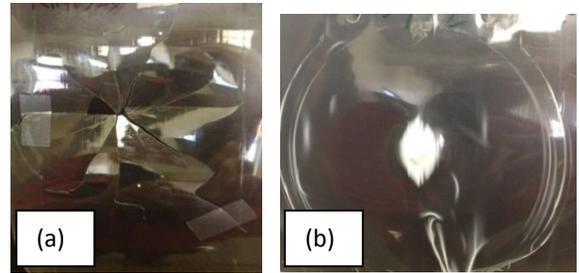
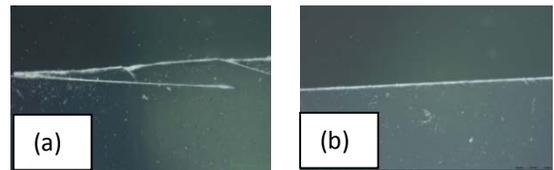


Fig. 8 Photographs of cut edge of 15 mil sheet containing (a) 0 and (b) 5% a-PHA



The effect of a-PHA addition to PLA blown films has also been evaluated at different a-PHA addition rates. Not only does the addition of a-PHA to PLA films improve the dart drop strength, it also significantly increases the tear strength as shown in Table 1. The increase in tear strength again demonstrates a reduction in PLA notch sensitivity.

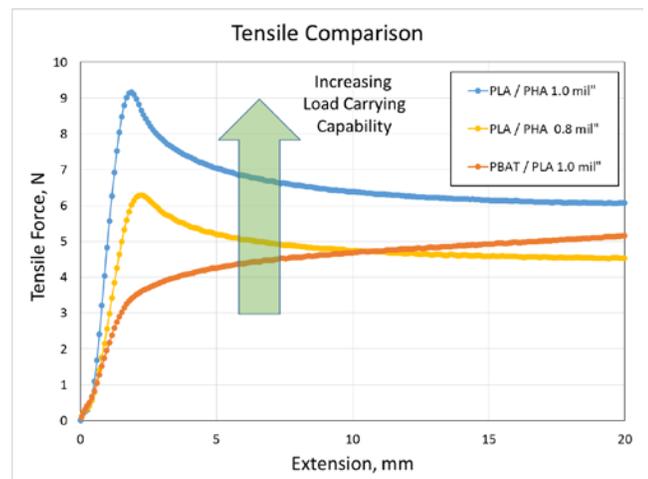
The level of a-PHA significantly improves the softness and flexibility of PLA films by as much as one third resulting in a reduction in the dead fold characteristics than can often lead to permanent creasing and visual spoilage of the PLA film or package.

One further attribute of a PLA/a-PHA blend is to increase the load carrying capability of a film or bag. Even at a 30 phr addition rate, the tensile modulus of the film is still of the order of 1000 MPa but can still be extended to >200% before breaking. A higher tensile yield strength means a higher load can be applied before yielding of the film or bag will occur. This facilitates the opportunity for potential down gauging compared to PBAT rich formulations that result in a lower yield strength. This is shown in Figure 9.

Table 1. Effect of PHA addition rate on Dart Drop and Tear strength of modified PLA films.

aPHA %	5	10	20	30	35
Dart impact (g)	-	-	35	239	421
MD Tear (g/mil)	11	15	31	72	56
TD Tear (g/mil)	13	16	45	150	179
MD modulus (MPa)	2759	2319	1657	973	709
TD modulus (MPa)	2651	2444	1453	1000	806
MD yield strength (MPa)	-	-	46	27	22
TD yield strength (MPa)	-	-	34	25	20
MD tensile strength (MPa)	65	59	35	39	42
TD tensile strength (MPa)	50	45	30	28	26
MD elongation (%)	3	4	143	142	140
TD elongation (%)	3	4	163	157	117
	Brittle Failure			Ductile Failure	

Figure 9. Effect of tensile yield strength on load carrying capability for PLA/a-PHA blends compared to a PBAT/PLA blend.



The tensile yield strength and modulus of the PLA/a-PHA film is close to that of HMWt HDPE as shown in Table 2. Whereas it is possible to increase the tensile yield strength of a PBAT/PLA film by increasing the level of PLA, it is found that this will result in a significant decrease in the tear strength which is not the case with the PLA/a-PHA film.

Table 2. Tensile yield strength of PLA/a-PHA films compared to a PBAT/PLA film, a LDPE Film and a HMWt HDPE film.

	Units	LDPE** (typical)	PBAT/ PLA*	PLA/ a-PHA*	HDPE*** (typical)
Melt index	g/10 min 2.16 kg @ 190°C	2.0	2.5	2.0	0.06
MD Tear	g/mil	350	250	200	11
Dart impact	g/mil	110	300	275	340
Tens. Yield Strength	MPa	16	15	32	34
Tensile Modulus	MPa	183	445	1200	945

* Data of Metabolix 1.0 mil

** Data of NA952-000 1.25mil LDPE from LyondellBasell

*** Data of L5005 0.5 mil HDPE from LyondellBasell

Pellet blends of PLA and a-PHA masterbatches do not require intensive mixing to achieve homogeneous properties. Pellet blends were injection molded with a screw devoid of a mixing section and using low back pressure. Blending a-PHA masterbatches with PLA and feeding to single screw film or sheet extruders has also been successfully carried out.

Technical guides for melt processing of Mirel masterbatches are available from Metabolix, Inc.

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