

Poly(lactic acid) and Polyamide 11 with controlled macromolecular architecture: synthesis and characterization

G. Di Silvestro^a, M. Ortenzi^a, H. Farina^a, C.M. Yuan^a, L. Basilissi^a, E. Zini^b, L. Martino^b and M. Scandola^b

a) University of Milan, Department of Organic and Industrial Chemistry, Via Venezian 21, 20133 Milan (Italy)

b) University of Bologna, Department of Industrial Chemistry, Viale del Risorgimento 4, 40135 Bologna (Italy)

The interest towards environmentally friendly polymers has been growing in the last decade and, especially in these last years, a strong effort has been made to find adequate substitutes for "traditional" oil-derived polymers.

PLA and PA11 are two examples of polymers of this kind; they both derive from renewable sources (PLA derives from corn or sugar and PA11 derives from castor) and PLA is biodegradable according to ASTM standard test.

PLA and PA11 present on the market are linear polymers and just a few works are present about complex architecture PLA and PA11 obtained with bulk polymerization; in this work some samples were synthesized using different multifunctional comonomers in order to modify macromolecular architecture.

Experimental Part

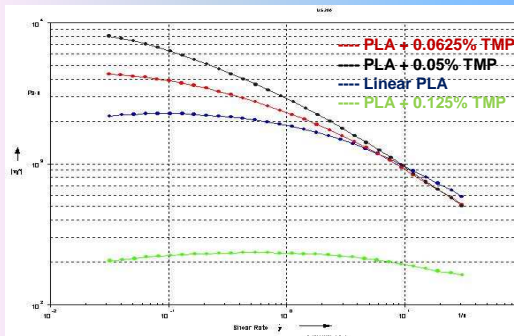
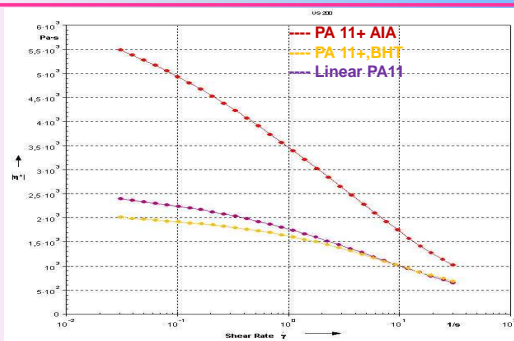
PLA was obtained via bulk Ring Opening Polymerization (ROP) of lactide at 190°C for 2 hours under nitrogen using Sn(Oct)₂ as catalyst.

PA11 was synthesized in bulk at 270°C for 4 hours under nitrogen atmosphere.

Low quantities of different multifunctional comonomers were directly added in the feed in order to obtain polymers with different macromolecular architecture.

PLA/PA11 blends were prepared mixing different amount of the two homopolymers.

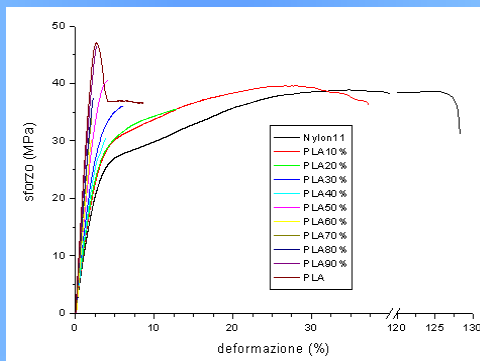
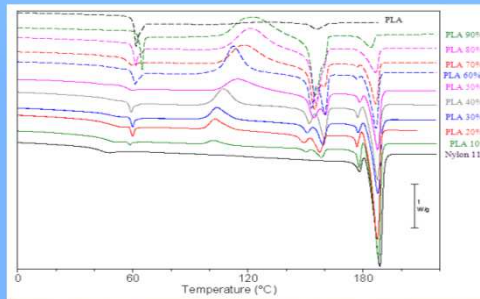
PLA present in blends is able to crystallize in quantities much greater than PLA homopolymer. Nylon 11 crystallizes both in blends than in homopolymer with a considerable amounts of enthalpy and its melting heat decreases with increasing amounts of PLA.



Using different type and amount of comonomers is possible to change the melt behavior of PLA and PA11.

Rheologic analyses demonstrate that as long as DP_n in star polymer is near the ones of linear polymers, melt viscosity is far lower, but when a very high DP_n is obtained, melt viscosity significantly increases.

Branched polymer is more viscous than the linear one, as expected.



The mechanical behavior of the two homopolymers is very different. The PLA has a strength value of 2.5% and breaks for deformation of about 10%. Nylon11 is much more ductile: the module is approximately halved the strength value is much higher ($\epsilon_y = 35\%$) and the rupture occurs at deformations higher than 100%. A curve very similar to that of Nylon 11, even if with less elongation and higher elastic modulus is the blend containing 10% PLA. All other blends richer in PLA show a brittle behavior and break before the yield point.

f (PLA)	E (MPa)	DS(E)	ϵ_b (%)	DS(ϵ_b)	σ_b (MPa)	DS(σ_b)
0	1006	36	35.8 ^{a)}	2.6	38.8 ^{a)}	1.0
0.1	1140	34	28.4 ^{a)}	2.4	40.7 ^{a)}	1.9
0.2	1223	61	13.0	3.4	35.2	1.1
0.3	1417	80	5.7	0.9	35.3	0.6
0.4	1377	44	4.1	0.5	30.0	2.5
0.5	1613	67	4.0	0.3	38.9	1.5
0.6	1811	72	2.6	0.4	34.6	2.9
0.7	1955	67	2.3	0.3	35.7	1.8
0.8	2053	32	2.7	0.3	41.3	3.2
0.9	2276	117	2.8	0.2	47.5	2.8
1	2341	93	2.5	0.3	43.5	5.6

Conclusions

- ✓ Rheological curves show a marked dependence of viscosity on the quantity and nature of the comonomers
- ✓ In PLA/PA11 blends nylon 11 crystals that form during rapid cooling in the press act as heterogeneous nucleating agents that increase the speed of crystallization of PLA during the DSC analysis.
- ✓ Blends obtained by hot mixing in which PLA is present only in the amorphous phase behave like systems with good mechanical compatibility.