

Nanocomposites and nanomaterials

Structural modification of poly(DL-lactic acid) material by equal-channel multi angular extrusion

Bondarenko V., Voznyak A.V.

Faculty of Physics and Mathematics, Kryvyi Rih State Pedagogical University. Gagarin av. 54, 50086, Kryvyi Rih, Ukraine

E-mail: avvoznyak76@gmail.com

Introduction

Poly(lactide) (PLA) is a biodegradable and renewable thermoplastic considered as the most promising biopolymer for its excellent biodegradability, biocompatibility, and good mechanical properties. However, despite indisputable advantages, several weaknesses, such as, the inherent brittleness and low impact resistance as well as low thermal stability limit the advantage of PLA in industrial use. To improve the properties of PLA, various strategies have been proposed, such as, plasticization, copolymerization, the formation of blends and composites based on it. In every case, the properties of the obtained PLA-based materials correspond to the so-called mixture rule, when they are the arithmetic mean of the properties of each of the components. Therefore, one can enhance the toughness or strength of the PLA matrix material unilaterally. In the present work, equal channel multi angular extrusion (ECMAE) was selected as an extrusion method to obtain PLA with superior mechanical properties. This kind of processing is also able to form a reinforcing structure characterized by enhanced strength and toughness, without the need for the introduction of nanofillers, the formation of blends, and so on. The effect of the arm length of PLA (linear vs long chain branched structure) on the mechanical properties of the system self-reinforced PLA was also discussed.

Solid state extrusion

A polymer billet was pressed through a device consisting of several pairs of channels of the same diameter intersecting at varied angles Θ_i . The inlet and outlet channels are made vertically coaxial to keep the billet pointing to the right direction. ECMAE was carried out at the deformation intensity $\Delta\Gamma = 0.83$, the accumulated strain $e = 8.5$, the deformation route $D + C$, the extrusion temperature of 160 C and at the extrusion rate of 0.6 mm/s followed by cooling the extrudates in air at room temperature. The above-mentioned processing conditions allowed for the generation of the maximal chain orientation of the PLA during ECMAE. It should also be noted that the high extrusion temperature T_e allowed not only to achieve maximum degrees of molecular orientation, but also to obtain high thermal stability of the extrudates, since, annealing the extrudates at temperatures $(0.9-1.0) T_e$ does not lead to a deterioration of their mechanical properties.

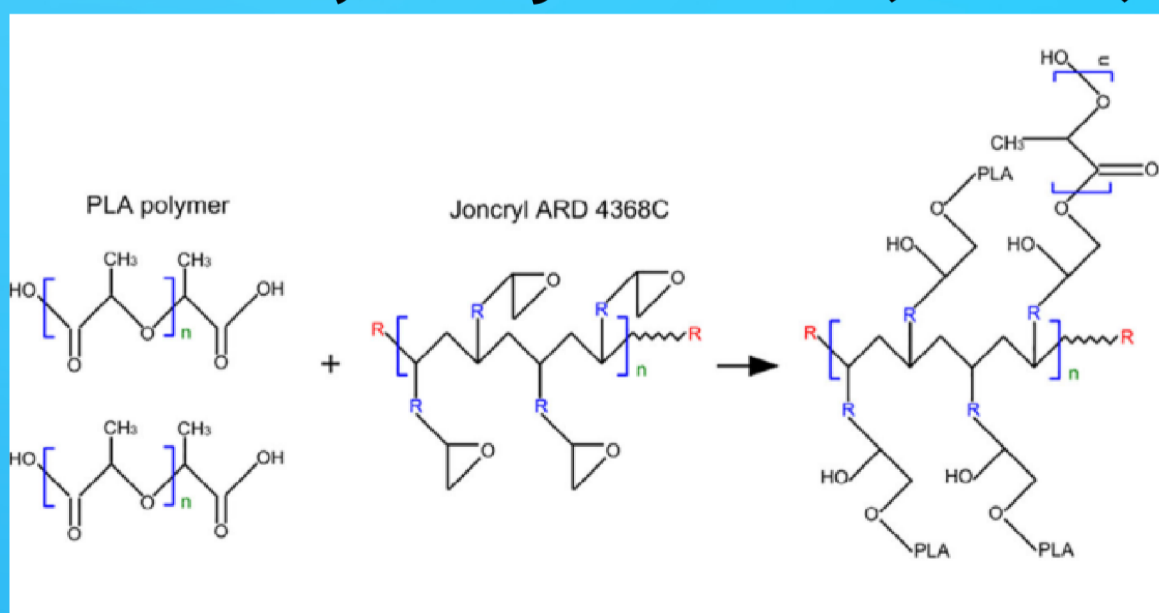
Materials

Poly(lactic acid) (PLA) 4032D was purchased from NatureWork LLC. It exhibited a weight-average molecular weight of 19,600 kDa and polydispersity of 1.89 as determined through gel permeation chromatography. The multifunctional epoxide chain extender Joncryl ADR-4368C was supplied by BASF. Its molecular weight was 6800 Da with the epoxy equivalent weight of 285 g/mol.

Formation of branch structure

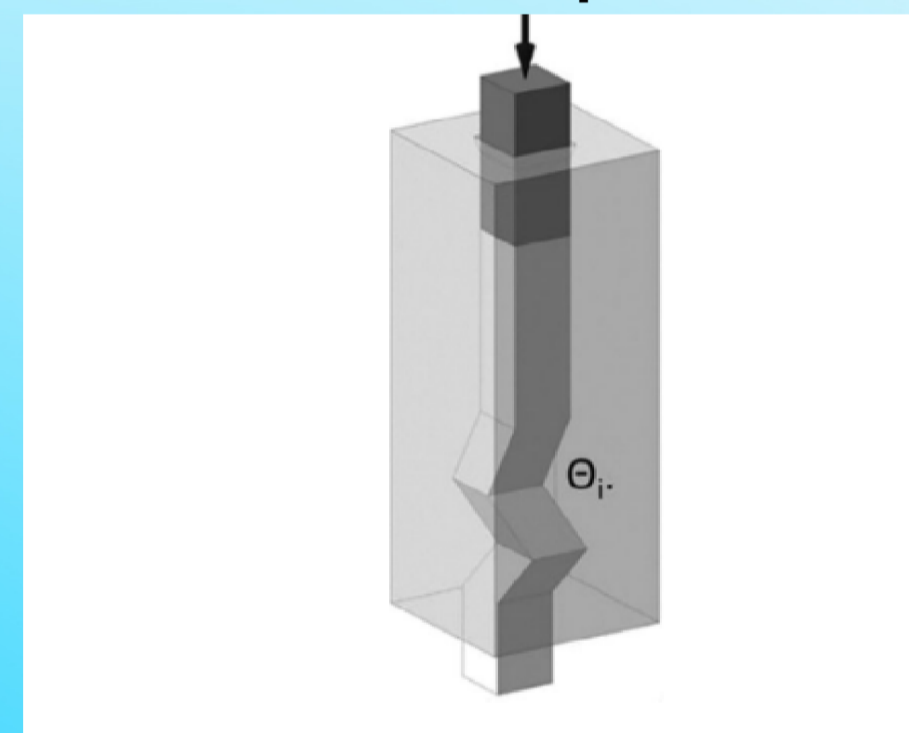
To create a branched structure, the initial PLA was first milled into powder on a laboratory grinder, dried under the same conditions, and then mixed with the reaction modifier Joncryl. The creation of a branched structure was judged by the dependence of a melt flow index (MFI) on temperature. The initial linear PLA is referred to L-PLA and long chain branched PLA - LCB-PLA.

Reaction of Joncryl with PLA (scheme)



Material	Temperature, C	MFI, g/10 min/2.16 kg
L-PLA	200	3.9
	210	7.5
LCB-PLA	200	0.23
	210	0.27

Scheme of equal-channel multiple-angular extrusion process



Thermal properties of L-PLA and LCB-PLA

Material	Melting enthalpy ^a , J/g		Degree of crystallinity, %		Low melting temperature (β form), C		High melting temperature (α form), C	
	Initial	ECMAE	Initial	ECMAE	Initial	ECMAE	Initial	ECMAE
L-PLA	60.2	64.3	64	69	155	—	169	171
LCB-PLA	46.8	52.7	50	56	151	—	164	169

^aMelting enthalpy of 100% crystalline PLA is 93.7 J/g.

Mechanical properties of the L-PLA and LCB-PLA

Material	Young's modulus, GPa		Yield strength, MPa		Strain at break, %		Impact strength, kJ/m ²	
	Initial	ECMAE	Initial	ECMAE	Initial	ECMAE	Initial	ECMAE
L-PLA	3.19 ± 0.12	4.02 ± 0.14	50 ± 2	56 ± 3	5.6 ± 0.3	12.2 ± 0.5	55 ± 2	77 ± 4
LCB-PLA	3.02 ± 0.13	3.26 ± 0.12	46 ± 2	50 ± 2	15.0 ± 0.5	13.5 ± 0.5	70 ± 3	82 ± 3

CONCLUSION

ECMAE technology is applied to demonstrate the possibility of simultaneously increase the modulus, strength, and ductility of PLA. The role of ECMAE in the formation of the orientational order, an increase in the degree of crystallinity and the creation of more perfect a crystals is revealed. The effect of two types of PLA with linear and branched morphology on the magnitude of the effects achieved is considered. It is shown that the highest effect is achieved in the case of a linear PLA. ECMAE results in 12%, 26%, 217%, and 40% increase in tensile strength, Young's modulus, strain at break and impact strength, respectively for linear PLA, while in the case of a long chain branched PLA, the growth of tensile strength, Young's modulus and impact strength is only 9%, 8%, and 17%, respectively. ECMAE-modified PLA also has better thermal stability.