

Stretchability and Deformation Behavior of Polybutylene Adipate-co-terephthalate Blend Films

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Abstract

The single use packaging is widely used in various products; ranging from food to non-food contact, from commodity to specialty purposes. Most of these materials are derived from non-renewable fossil resources. In a sustainable manner, it needs to be recyclable or compostable. Good mechanical properties together with biodegradability can make the product more recyclable. In this study, the elasticity for films consisting of polybutylene adipate-co-terephthalate (PBAT) blended with polylactic acid (PLA) (10, and 20 %wt), additive and reactive agents were evaluated. The blends were prepared via a twin-screw extruder. The film specimens were prepared by cast film extrusion. The films were then stretched with different ratios (1.5, 2 and 2.5 times) by the uniaxial machine. The mechanical properties, elasticities and surface morphology of uniaxially stretched PBAT and PBAT blend films were characterized by tensile testing and scanning electron microscope (SEM), respectively. The tensile strength of stretched films tended to improve while the elongation at break reduced at higher stretching ratios. The surface morphology of stretched films revealed that the degree of orientation was increased after higher stretching ratios. The ability to recover in the plastic deformation region of stretched films was increased at the higher stretching ratios.

Keywords: Elasticity, Polybutylene adipate-co-terephthalate, Biodegradable plastics, Stretchability

1. Introduction

Nowadays most of the food and non-food packages are made from fossil-based polymers such as poly(propylene) (PP), high density poly(ethylene) (HDPE), low density poly(ethylene) (LDPE), linear low density poly(ethylene) (LLDPE), poly(ethylene terephthalate) and etc. These plastics, particularly the single use plastic, are generally not biodegradable and accumulate for a very long time. Based on the single-use plastic waste statistics, 380 million tons of single-use plastic (or 50% of the total plastic production) were generated each year and we use them only once, the same amount of plastic becomes trash in a year (SeedScientific, 2021). Regarding the single-use plastic packaging, the thin films are most dominated in terms of the applications both for food and non-food items. It is interesting therefore to find sustainable solutions. Two of the main options are

recycle or composting options for such a plastic. For composting options, the existing compostable polymers poly polybutylene adipate-co-terephthalate (PBAT), polylactic acid (PLA), and poly(butylene succinate) (PBS) are the most popular ones. In 2020, global production capacities of biodegradable polymer were more than bio-based/non-biodegradable polymers. Top 3 of biodegradable polymers are Starch blends, PLA and PBAT, respectively (European Bioplastics, 2020). In the packaging use, PBAT is generally considered the most suitable alternative to low-density polyethylene based products due to its properties similar to LDPE and because of its high molecular weight and long chain branched molecular structure, high elongation at break, high failure energy and good processability on blown and cast film lines (BASF, 2013; Pietrosanto, Scarfato, Di Maio, & Incarnato, 2020).

In recent years, the research development and improvement of PLA and PBAT have been popular in many applications (Chen, Han, Zhang, & Dong, 2021; Deng, Yu, Wongwiwattana, & Thomas, 2018; Hongdilokkul et al., 2015; Li et al., 2017; Su, Duhme, & Kopitzky, 2020). Su et al. (2020) prepared uncompatibilized PBAT/PLA blends with different techniques. In blown films production, using PLA contents (10-30 %wt), the tensile strength of blown films tended to increase in MD while the elongation at break increased. However, the tensile strength of pressed panels and flat films processes were not different except 30 %wt PLA in the pressed panels process, which decreased. For the same composition, the mechanical properties of blown film production were higher than pressed panels. Hongdilokkul et al. (2015) used peroxide as a reactive agent in PLA/PBAT blends. They reported an improved interfacial adhesion between PLA and PBAT phase, leading to the improvement of the drawability. When blended with 20 %wt PBAT, the drawability, processability and toughness properties of PLA were greatly improved. Likittanaprasong, Seadan, and Suttiruengwong (2015) enhanced impact property of poly(lactic acid) with different flexible copolymers. They used 6 flexible copolymers. When copolymers were added into PLA, tensile strength and modulus of PLA/copolymers were decreased as a result of elasticity of copolymers. PLA/copolymers were more flexible than PLA. The elongations at break of PLA/copolymers were increased resulting from the PLA/copolymers samples more ductile than PLA sample. The results indicated that different copolymers had different impact resistance. Chen et al. (2021) prepared toughened PLA nanocomposites by combining the modification nano-SiO₂ and pre-stretching. The modulus and tensile strength of PLA/SiO₂ nanocomposites were higher than those of pure PLA because SiO₂ nanoparticles played a reinforcement role in the PLA matrix. After pre-stretching, a brittle-to-ductile transition occurred in the PLA/SiO₂ nanocomposites. When the pre-stretching ratio (PSR) was 0.5, 1.0, 1.5 and 2.0, the elongation at break, modulus and tensile strength at break were higher than undrawn PLA. The

elongation at break was decreased with increasing PSR while modulus and tensile strength at break were increased greatly. This was due to the degree of orientation, which was increased with the increment of PSR. Thus, in this work, we proposed another way of improving the mechanical properties of PBAT and PBAT blend films by stretching method. The effect of stretching on the mechanical properties, elasticity and surface morphology of PBAT and PBAT blend films were investigated.

2. Materials and Methods

2.1 Materials

PBAT grade Ecoflex® F Blend C1200, BASF was purchased from Polymat Ltd. PLA grade 4043D was purchased from NatureWorks. Di (tert-butylperoxyisopropyl) benzene (DB), Perkadox 14s, having 40% of peroxide, was supplied by Akzo Nobel, Netherlands. Multi-functional epoxy chain extender (ECE), Joncryl® ADR-4368C was purchased from BASF Co. Ltd. Ethylene copolymer (E) (Biomax® strong 120) was purchased from Dupont CO. Ltd.

2.2 Methods

2.2.1 Preparation and stretching of films

The PBAT/PLA blended with additive and reactive agent was prepared by a twin-screw extruder. The melting blending process was carried out at temperature profile of 80-190°C with a screw speed of 200 rpm except neat PBAT and PBAT_E5. Both compounds were carried out at 80-135°C with the same screw speed as the PBAT/PLA blends. The compositions of polymer compounds were shown in table 1. The compound films were prepared by a cast film extruder. The cast film extrusion process was carried out at 105-150°C (neat PBAT and PBAT_E5) and 110-210°C (PBAT/PLA blended with additive and reactive agent) with screw speed 80 rpm. Then the stretched films were fabricated with 1.5, 2 and 2.5 times of original length by a uniaxial machine as shown in Figure 1. The stretching temperature was provided at ~60°C by heat gun. After stretching, they

were cooled down to room temperature by air before they were unloaded from the grips.



Figure 1. Uniaxial machine.

Table 1. The composition of polymer compounds.

Samples	PBAT	PLA	Ethylene copolymer (phr)	DB (phr)	ECE (phr)
PBAT	100	-	-	-	-
PBAT_E5	100	-	5	-	-
P90_L10_DB0.2_ECE0.1	90	10	-	0.2	0.1
P90_L10_E5_DB0.2_ECE0.1	90	10	5	0.2	0.1
P80_L20_DB0.2_ECE0.1	80	20	-	0.2	0.1
P80_L20_E5_DB0.2_ECE0.1	80	20	5	0.2	0.1

of 30 MPa and a crosshead speed of 50 mm/min. The specimens of unstretched and stretched were cut the same as tensile testing.

2.2.4 Scanning electron microscopy (SEM)

Surfaces morphology of the samples were investigated by a Field Emission Scanning Electron Microscope, FESEM) MIRA3 TESCAN CO., LTD, Czech Republic. Gold sputtering was performed to coat on samples before testing.

3. Results and Discussions

3.1 Mechanical properties

The mechanical properties of unstretched PBAT, PBAT_E5 and PBAT/PLA blend films were measured by tensile testing at room temperature. Figure 2. showed the stress-strain curves of unstretched PBAT, PBAT_E5 and PBAT/PLA blend films. Unstretched PBAT film showed tensile strength and elongation at break at 25.4 MPa and 551.29%, respectively. When adding ethylene copolymer, tensile strength of unstretched PBAT_E5 film decreased from 25.4 MPa to 21.9 MPa while elongation at break slightly increased from 551.29%

2.2.2 Tensile testing

The mechanical properties of samples were measured at room temperature with a crosshead speed of 50 mm/min by a universal testing machine (NRI-TS500-5B) according to ASTM D882. The standard films were cut from the unstretched and stretched samples along the stretching direction

2.2.3 Cyclic testing

Elasticities of the samples were measured by a universal testing machine in cyclic test mode. The cyclic tests were performed at maximum stress (σ_{max}),

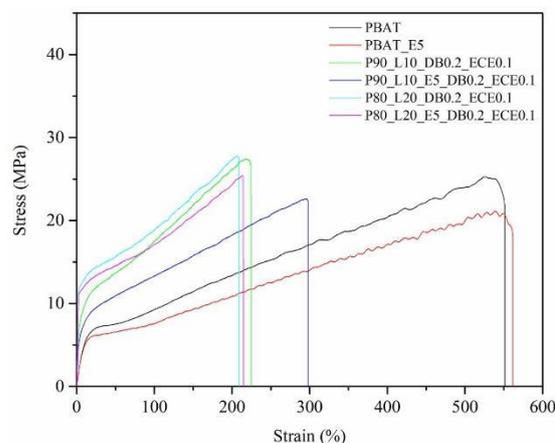


Figure 2. Stress-Strain curve of unstretched PBAT, PBAT_E5 and PBAT/PLA blend films.

to 561.89%. For PBAT/PLA blend films, elongation at break of PBAT/PLA blend films was decreased a lot after blending PLA into PBAT while tensile strength slightly increased except tensile strength of P 90 _L10 _E 5 _ DB 0.2 _ ECE 0.1 film slightly decreased. When compared neat PBAT film with P90_L10_DB0.2_ECE0.1 and P80_L20_DB0.2_ECE0.1 films, tensile strength increased from 25.4 MPa to 27.4 MPa and 27.8 MPa respectively,

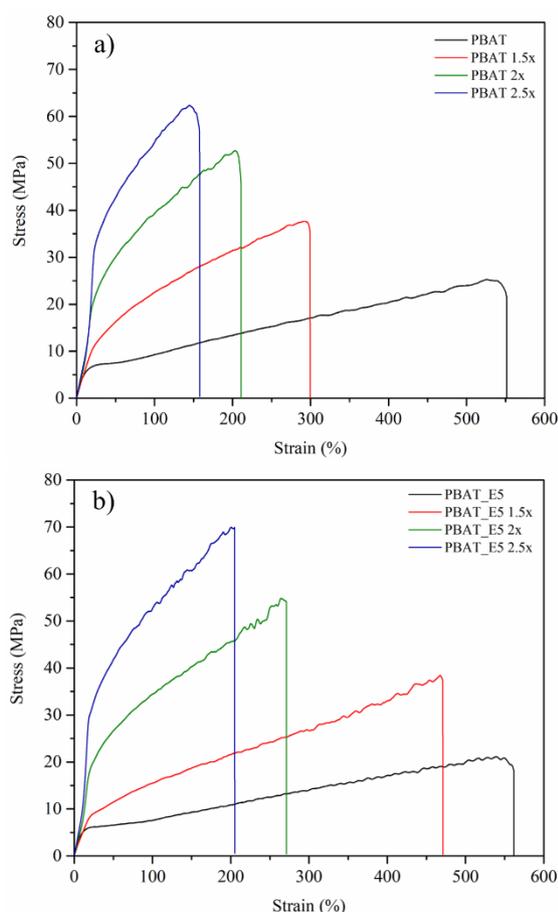


Figure 3. Stress-Strain curve of unstretched films and stretched films (1.5x, 2x and 2.5x) a) PBAT and b) PBAT_E5.

whereas elongation at break was decreased from 551.29% to 224.65% and 209.08% respectively because PLA is rigid polymer when compared to PBAT. Rigid polymer has high tensile strength and modulus (Pitivut, Suttiruengwong, & Seadan, 2015). When comparing PBAT/PLA blend films with and without additive, tensile strength of P90_L10_E5_DB0.2_ECE0.1 and P80_L20_E5_DB0.2_ECE0.1 decreased from 27.4 MPa and 27.8 MPa to 22.6 MPa and 25.4 MPa respectively while elongation at break increased from 224.65% and 209.08% to 298.13% and 214.51% respectively because ethylene copolymer was more flexible than PLA (Likittanaprasong et al., 2015). Tensile strength of all unstretched films was slightly different but elongation at break of unstretched PBAT/PLA blends film was significantly decreased. Therefore, unstretched PBAT and PBAT_E5 films were

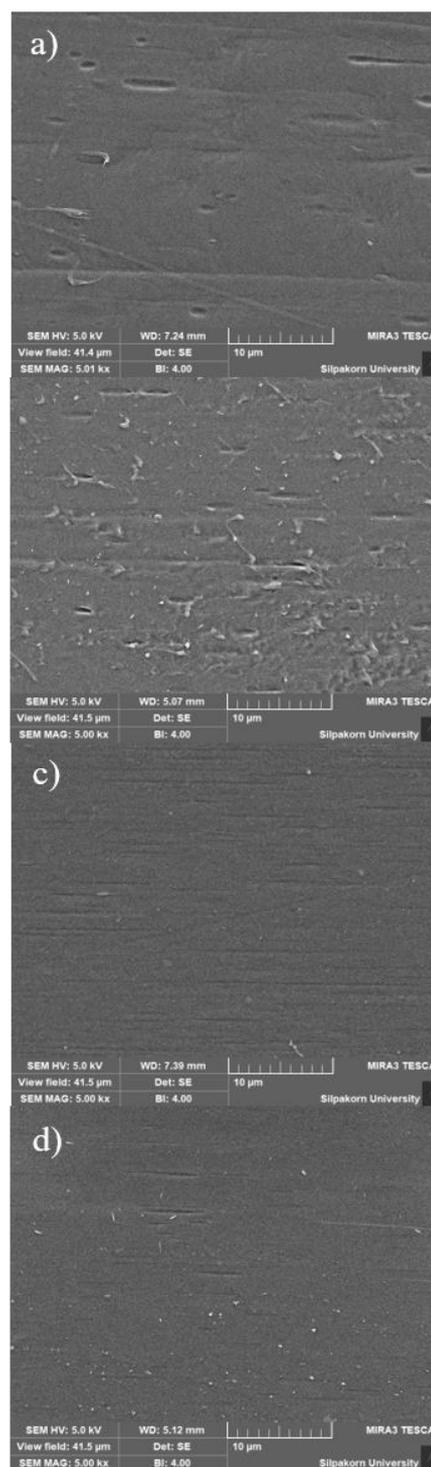


Figure 4. Surface morphology of unstretched films a) PBAT and b) PBAT_E5 and stretched films (2x) c) PBAT 2x and d) PBAT_E5 2x.

selected for stretching to improve mechanical properties and studied elasticity after stretching.

After stretching PBAT and PBAT_E5 films, Figure 3. represents the stress-strain curves of

unstretched and stretched PBAT and PBAT_E5 films with different ratios. It was obvious that the tensile strength of stretched PBAT and PBAT_E5 films were different after stretching. With increasing the stretching ratio, the stretched PBAT and PBAT_E5 transformed from a ductile to brittle behavior and tensile strength of stretched PBAT and PBAT_E5 films tended to increase while elongation at break tended to decrease because of stretched films in the cold drawing zone of polymer and the orientation of the polymer chains during in stretching process (Su et al., 2020). At the highest stretching ratio (2.5x), tensile strength of stretched PBAT and PBAT_E5 films increased by 164% (from 25.4 MPa to 66.71 MPa) and 186% (from 21.9 MPa to 63.22 MPa) but elongation at break decreased by 71% (from 551.29% to 165.19%) and 63% (from 561.89% to 206.15%), respectively. This may be due to the fact that by stretching, the stretched polymers chains were oriented along uniaxial machine direction and the degree of orientation was increased with the increment of stretching ratio (Chen et al., 2021).

3.2 Morphology of unstretched and stretched films

Figure 4. shows Surface morphology of unstretched and stretched PBAT and PBAT_E5 films with stretching ratio 2x. Surface morphology of unstretched PBAT and PBAT_E5 films show droplet voids on film surfaces were illustrated in Figure 4 a) and b). But unstretched PBAT and PBAT_E5 showed different film surfaces. When adding ethylene copolymer into PBAT, film surface of PBAT_E5 film was rougher than PBAT film because ethylene copolymer particles were elongated and dispersed on the film surface After stretching PBAT and PBAT_E5 films. Surface morphology of stretched PBAT and PBAT_E5 were shown in figure 4 c) and d), the droplet voids became elongated void due to the orientation of the stretched films in uniaxial machine direction. It confirmed the increased degree of orientation with the increment of stretching ratio, resulting in tensile strength of stretched films increased while elongation at break decreased as mentioned above. The increase in tensile strength may be resulted from the degree of the crystallinity. However, a role of the crystallinity was not investigated in this work.

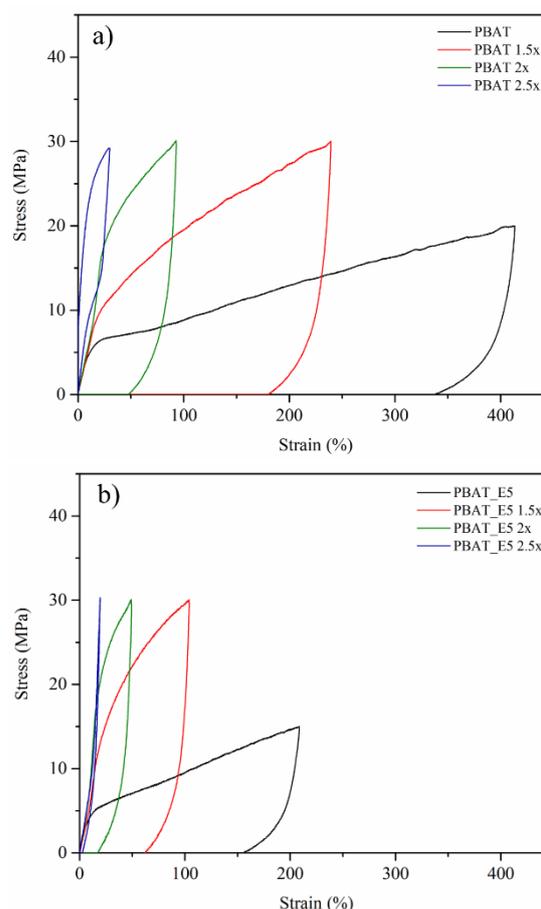


Figure 5. Stress-Strain curve from cyclic test of unstretched films and stretched films (1.5x, 2x and 2.5x) a) PBAT and b) PBAT_E5.

3.3 Elasticity of unstretched and stretched films

Elasticity of unstretched and stretched PBAT and PBAT_E5 films were tested by cyclic testing. It was reported in the form of %recovery. The cyclic tests were performed at maximum stress 30 MPa. Figure 5. showed the stress-strain curves from cyclic tests of unstretched and stretched PBAT and PBAT_E5 films. In case of unstretched PBAT and PBAT_E5 films, they cannot be tested at maximum stress 30 MPa because tensile strength of unstretched PBAT and PBAT_E5 films were 25.4 MPa and 21.9 MPa, respectively. The unstretched PBAT and PBAT_E5 films were tested at maximum stress 20 MPa and 15 MPa, respectively. It found that %recovery of unstretched PBAT and PBAT_E5 films were 18.09% and 25.25%, respectively. After stretching, %recovery of stretched PBAT and

Table 2. %Recovery of unstretched and stretched PBAT and PBAT_E5 films.

Sample	Stretching ratio	Recovery (%)
PBAT	1	18.09
PBAT 1.5x	1.5	24.80
PBAT 2x	2	48.41
PBAT 2.5x	2.5	74.24
PBAT_E5	1	25.25
PBAT_E5 1.5x	1.5	40.11
PBAT_E5 2x	2	64.64
PBAT_E5 2.5x	2.5	86.15

PBAT_E5 films increased with increasing stretching ratio because increment of stretching ratio resulted in tensile stress of stretched films equal to 30 MPa at lower %strain. At lower %strain, film showed higher elasticity than at higher %strain because when the film was drawn continuously, the film entered more deformation zones. Thus, the film possessed higher strength.

4. Conclusions

The stretching process can improve mechanical properties and elasticity as indicated by tensile strength of PBAT and PBAT_E5 films increased by 164% and 186% but elongation at break decreased by 71% and 63% respectively when stretching at the highest ratio (2.5x) due to stretched films are oriented along the uniaxial machine direction and the degree of orientation increased. The elasticity shows in the form of %recovery. %Recovery of stretched PBAT and PBAT_E5 increased when stretching at the highest ratio due to elasticity of films increased. SEM shows surface morphology of stretched PBAT and PBAT_E5 which indicates the longer elongated voids when stretching. It confirmed stretched films are oriented along the uniaxial machine direction. More work needs to be carried out to ensure the application including the coefficient of friction, the shelf-life and the economics analysis of the products.

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