MODIFICATION OF POLY(LACTIC ACID) BY BLENDING WITH POLY(METHYL METHACRYLATE-CO-ETHYL ACRYLATE) FOR EXTRUSION BLOW MOLDING APPLICATION

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Abstract

The current paper investigates the influence of poly(methyl methacrylate-co-ethyl acrylate) (PMMA-co-EA) content on the flow, mechanical, thermal and morphological properties of poly(lactic acid) (PLA). Mechanical test results indicated that the blends were softer and tougher due to the decreased tensile and flexural strengths and the increased elongation at break and impact resistance. With the presence of PMMA-co-EA, regions of amorphous were found to increase together with the decreased degree of crystallinity at all blend compositions. Rheological properties indicated that molten PLA/PMMA-co-EA blends were more viscous in both under shear and applied load, which suitable for the blow molding process. At 10 wt%, the increased shear viscosity and decreased melt flow index (MFI) were around 240 and 63% respectively. PMMA-co-EA provided good bottle blown product at 10 wt%. Less than this concentration, some flaws were clearly observed.

Keywords: Biodegradable polymers, Mechanical properties, Rheological properties, Thermal properties, Extrusion blow molding.

Nomenclatures

T_c	Crystallization temperature, ^{o}C
T_g	Glass transition temperature, ^{o}C
T_m	Melting temperature, ^{o}C
X_c	Degree of crystallinity, %
X_{PLA}	Mass fraction of poly(lactic acid)

Greek Symbols

ΔH_c	Enthalpy of crystallization, J/g
ΔH_f	Heat of fusion, J/g
ΔH_m	Enthalpy of melting, J/g

Abbreviations

ABS	Acrylonitrile Butadiene Styrene terpolymer
DSC	Differential Scanning Calorimeter
FE-SEM	Field Emission Scanning Electron Microscope
HDT	Heat Distortion Temperature
MFI	Melt Flow Index
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Poly(butylene succinate)
PBSES	Poly(butylene succinate-b-ethylene succinate)
PC	Polycarbonate
PEO	Poly(ethylene oxide)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PMMA-co-EA	Poly(methyl methacrylate-co-ethyl acrylate)
PVC	Poly(vinyl chloride)

1. Introduction

As a biodegradable polymer, poly(lactic acid) (PLA) has drawn much attention from both researchers and plastic product developers. Numerous advantages of PLA are widely known to have high strength, good processability, biodegradability and bio-compatibility [1-3]. However, several disadvantages still exist in the neat PLA such as low thermal stability, low impact resistance and poor melt viscosity [4]. These shortcomings have limited the processability of PLA in blow molded products such as bottle. PLA have been modified by many additives in order to obtain the PLA with high impact resistance [1-2], high thermal stability [5-6] and high melt viscosity [7-8].

Rheological property is an important parameter indicating the processability of PLA in many fabrication processes namely; blow molding, blown film, foaming, casting or thermoforming [9]. Especially in the extrusion blow molding, high blow pressure is usually applied to blow the parison until fully inflate the mold. This application requires PLA with high melt viscosity and high melt strength [4].

Incorporation of poly(methyl methacrylate-co-ethyl acrylate) (PMMA-co-EA) is widely known to improve the rheological behaviour and results in more homogeneous melt. High molecular weight of PMMA-co-EA also results in higher

melt strength. Many decades ago, PMMA-co-EA had been applied as a processing aid in petroleum-based polymers such as poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), Acrylonitrile Butadiene Styrene terpolymer (ABS) or polycarbonate (PC) [10]. Most of them are acrylic functional group compatibility [11-12]. Numerous papers indicated the compatibility and synergistic behaviours of PLA and the acrylic-based additives. They included acrylic core-shell rubber [1], poly(ethyl acrylate) [2] and styrene acrylic copolymer [3]. Thus, PMMA-co-EA seems to be one of appropriate rheological modifier for PLA due to its compatibility and high molecular weight.

To obtain PLA with desired flow and mechanical properties, many researchers had modified PLA with other macromolecules such as thermoplastic starch [13], poly(butylene adipate-co-terephthalate) (PBAT) [14], poly(butylene succinate) (PBS) [15], poly(ethylene oxide) (PEO) [12] and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [16]. Al-Itry et al. [14] found that blending PLA with PBAT exhibited higher viscosity and higher storage modulus. By using a torque rheometer, starch was found to increase the shear stress and the viscosity of PLA/starch blends at all compositions, following the power law model [17]. Singh et al. [4] found the increment of storage modulus, loss modulus and dynamic viscosity when nanoclay was added to PLA. At low frequency (1 rad/s), a slight improvement in the storage modulus was found due to the formation of percolating network structure. In this study, PLA was modified by PMMA-co-EA to obtain PLA with higher viscosity, good mechanical properties and good processability for extrusion blow molding process.
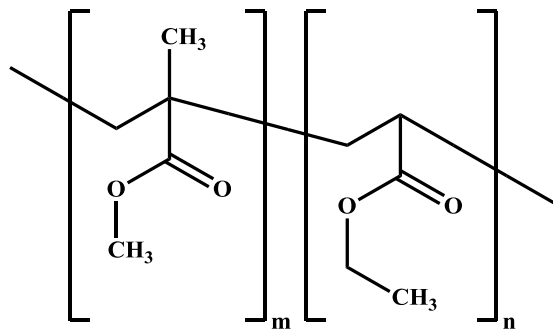

Fig. 1. Chemical structure of PMMA-co-EA.

2. Experimental Works

2.1. Raw materials

A blow molded bottle grade PLA (NatureWorks®, PLA7001D) was selected as a polymer matrix due to its biodegradability and commercial availability, which is generally applied for injection stretch blow molding process. It has density and melting point of 1.24 g/cm^3 and 155 ^{o}C respectively. Particles of PMMA-co-EA, with m:n ratio of 95:5, were supplied by Farrto Square Company Limited and applied to PLA for rheological modification purpose. Its density and average

particle size were 0.45 g/cm^3 and 150 nm respectively. Fig. 1 illustrates the chemical structure of PMMA-co-EA.
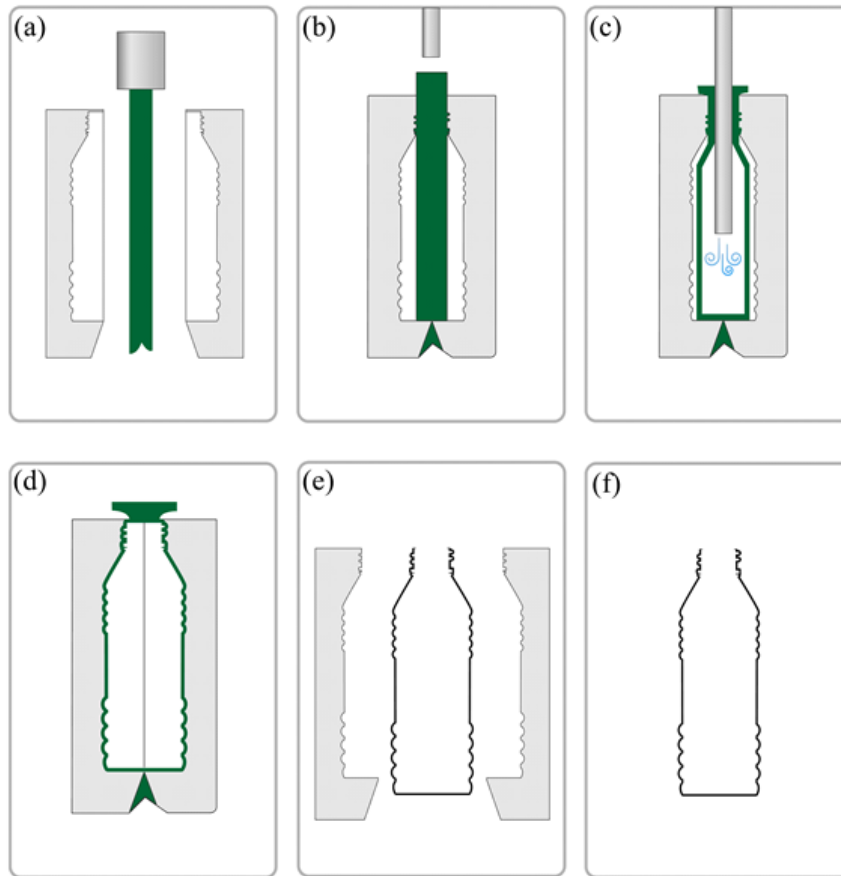

Fig. 2. Extrusion blow molding process.

2.2. Preparation of PLA/PMMA-co-EA blends

PMMA-co-EA was incorporated to PLA at four levels i.e. 1.0, 2.5, 5.0 and 10 wt%. Fabrication process of the blends began with dry-blending of PLA and PMMA-co-EA by using a hi-speed mixer (Thermo, Prism Pilot3) at the speed of 1000 rpm for 20 sec. This aimed to disperse PMMA-co-EA particles in PLA matrix prior to melt-blending. A twin screw extruder (Labtech, LTE16-40) was employed to melt-mixed PLA/PMMA-co-EA compositions at a screw speed of 100 rpm. The temperature profile along the extruder barrel from zone 1 to zone 5 was 165/175/180/185/185 ^{o}C respectively. The blends were then pelletized and injected to the test specimens by using a blade-type pelletizer and an injection molding machine. An extrusion blow molding machine (SMC 1500, SMC Corporation) was employed to fabricate the bottles from the modified PLA. To produce PLA bottles, six blow molding steps were clearly indicated in Fig. 2. In Fig. 2(a), a parison was dropped from an extruder and then the mold closed around parison, Fig. 2(b). After that the air was injected through parison until it

touched the wall of the mold to form bottle, Fig. 2(c). In Fig. 2(d) the excess polymer was removed. Finally, the mold was opened and the solidified part was removed, Fig. 2(e)-(f).

2.3. Testing and characterizations

2.3.1. Mechanical testing

Tensile test was conducted according to ASTM D638 by using a universal testing machine (INSTRON, 5567). Dumbbell type specimens were tested at a crosshead speed of 5 mm/min and at a pre-loading of 5 N. ASTM D790 was applied to measure the flexural properties of the blends under a three-point bending mode. A support span and cross head speed were set at 48 mm and 1.2 mm/min respectively. The Izod impact strength was evaluated by using an impact tester (Yasuda, 258Pc) following the procedure described in ASTM D256. All of the Izod impact test specimens were notched at an angle 45°. Five replicate specimens were tested and averaged for all the mechanical testing values.

2.3.2. Thermal characterizations

A Differential Scanning Calorimeter (DSC) (Perkin Elmer, DSC6000) equipped with an intra-cooler was carried out at a heating rate of 10 °C/min under nitrogen atmosphere. For the thermal history removal, the tested sample was firstly cooled down to -60 °C, isothermally held for 10 min, heated up to 210 °C and then isothermally kept for 10 min. For the cooling step, the test was conducted at a cooling rate of 10 °C down to -60 °C after the first heating run was completed. For the second heating run, the sample was re-heated up to 210 °C at the identical ramp rate. DSC was employed to investigate the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity (X_c) of the blends. X_c value was estimated from the second heating scan by using Eq.(1) [1-2,5].

$$X_C(\%) = 100 \frac{(\Delta H_m - \Delta H_c)}{\Delta H_f \times X_{PLA}} \tag{1}$$

where ΔH_m, ΔH_c and X_{PLA} are the enthalpy of melting, enthalpy of the crystallization and weight fraction of the PLA respectively. ΔH_f is the heat of fusion, defined as a melting enthalpy of 100 % crystalline PLA, which is 93 J/g [1-2, 5].

Heat distortion temperature (HDT) test was carried out under flexure stress of 18.6 kg/cm^2 in accord with ASTM D648 by using a heat distortion tester (Yasuda, HD-PC). Rectangular bars of each PLA and PLA/PMMA-co-EA blends were prepared with dimension of 13 mm in width, 3 mm in thickness and 127 mm in length.

2.3.3. Microscopic observation

The fracture surface morphology of PLA/PMMA-co-EA blends was observed by using a field emission scanning electron microscope (FE-SEM, Hitachi 4700e) at an accelerating voltage of 2 kV. Cryogenically fractured surface of each blend composition was mounted on an aluminium stub and sputter coated with a thin layer of gold before microscopic observations.

2.3.4. Rheological testing

Melt flow index (MFI) value was measured by using a melt flow indexer (MP993A, T. Olsen Ltd.) at 190 ^{o}C and a 2.16 kg load. The average of five test values was reported in each blend composition. Shear viscosity of the blends with various shear rates was measured by using a rheometer (HAAKE, Rheostress 600). A 25-mm parallel plate with a gap height of 2.5 mm was used. Test specimens were prepared by a compression molding machine at 180 ^{o}C. To observe the viscoelastic regime, shear rate sweep was set from 3 to 500 s^{-1}.

Table 1. Tensile properties of PLA and PLA/PMMA-co-EA blends.

Blend compositions	Tensile		
	Modulus (GPa)	Strength (MPa)	Elongation at break (%)
PLA	2.94±0.19	71.79±2.97	2.81±0.05
PLA/1.0wt%	2.87±0.58	67.36±3.40	5.03±0.49
PLA/2.5wt%	2.79±0.50	63.18±3.81	10.9±1.01
PLA/5.0wt%	2.74±0.51	60.09±3.92	15.8±2.18
PLA/10wt%	2.70±0.39	58.10±2.80	16.1±2.98

Table 2. Impact and flexural properties of PLA and PLA/PMMA-co-EA blends.

Blend compositions	Impact strength (kJ/m^2)	Flexural	
		Modulus (GPa)	Strength (MPa)
PLA	2.41±0.78	3.49±0.08	95.46±4.68
PLA/1.0wt%	2.97±0.76	3.34±0.70	90.30±3.67
PLA/2.5wt%	3.79±0.24	3.26±0.61	87.40±3.11
PLA/5.0wt%	4.51±0.90	3.08±0.33	85.91±3.58
PLA/10wt%	4.96±0.65	2.98±0.35	82.46±3.60

3. Results and Discussion

3.1. Mechanical properties and microscopic observation

Mechanical tests namely; tensile, flexural and impact of neat PLA and PLA modified with PMMA-co-EA were summarized in Tables 1 and 2. Adding flexible PMMA-co-EA was successfully increased the flexibility of PLA. Reductions of the tensile modulus and the tensile strength were observed due to the softening ability of PMMA-co-EA. Minimum value of the tensile modulus and the tensile strength were reached when PMMA-co-EA was added at 10 wt%. In this case, adding the acrylic copolymer to PLA matrix decreased the stress transfer ability from PLA to PMMA-co-EA [1-2]. The fracture behavior of PLA changed from brittle to ductile nature when PMMA-co-EA was added at least 2.5 wt%. Maximum increment in the elongation at break by more than 5 times was evidenced when the blend composition reached 10 wt%. The improvement in PLA toughness reflected as the increased impact strength. It reached the maximum value at 4.96 kJ/m^2, or two times higher than neat PLA, at 10 wt% PMMA-co-EA. Typically, significant improvement in the impact strength by around 2 to 3 times can be realized by using 10 wt% toughening agent [18]. This

implied that PMMA-co-EA played an important role in impact energy absorption upon impact force [1]. This correlated to the toughening mechanism induced by the PMMA-co-EA, which presented in Fig. 3.
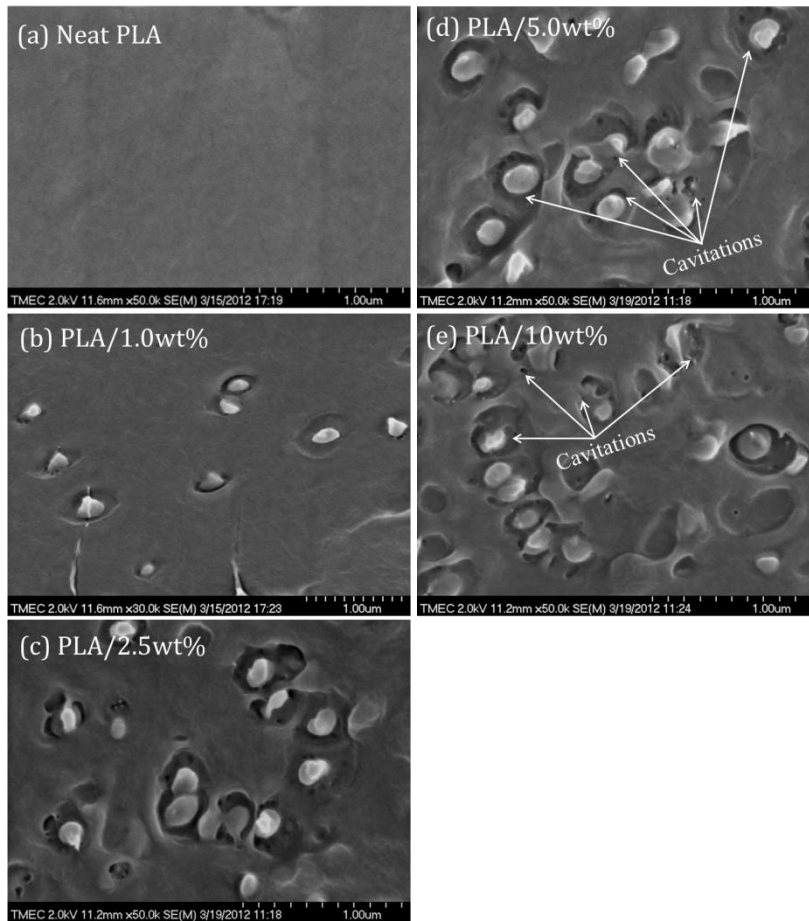

Fig. 3. FE-SEM micrographs of PLA and PLA/PMMA-co-EA blends.

FE-SEM micrographs of the cryogenic fractured surface of neat PLA and PLA with PMMA-co-EA were illustrated in Fig. 3. In Fig. 3(a), neat PLA showed a smooth fracture surface correlated to the rapid crack propagation. In Fig. 3(b) to (e), white round particles indicated PMMA-co-EA phases which deeply embedded and distributed in PLA matrix. With PMMA-co-EA, FE-SEM micrographs presented rougher fracture surface indicating that larger amount of energy required to break the specimen. In other polymer toughening systems, there are numerous toughening mechanisms proposed namely; crazing, cavitation, crack bridging and shear yielding which is the important energy dissipation processes involved in the fracture [1,14]. In this case, some cavitations caused by debonding were clearly observed in all PLA/PMMA-co-EA compositions. These cavitations were believed to be major factor of the improvement of impact resistance.
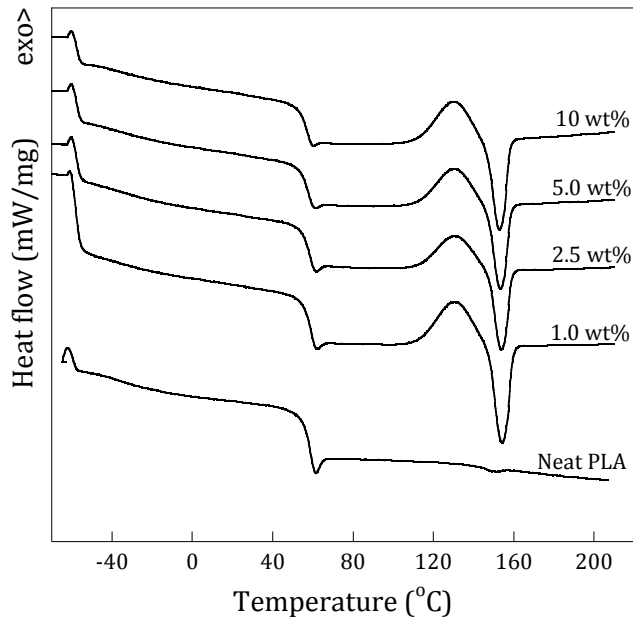
Fig. 4. DSC thermograms of PLA and PLA/PMMA-co-EA blends.

Table 3. Thermal properties of PLA and PLA/PMMA-co-EA blends.

Blend compositions	Transition temperatures (^{o}C)			X_c (%)	HDT (^{o}C)	MFI (g/10min)
	T_g	T_c	T_m			
PLA	61.22	120.3	154.8	2.37	60.26±0.59	21.58±4.38
PLA/1.0wt%	59.27	131.0	154.3	1.72	61.20±0.35	18.65±3.50
PLA/2.5wt%	57.79	131.5	153.0	0.26	60.88±0.79	13.30±3.85
PLA/5.0wt%	57.66	130.5	153.7	0.51	59.43±0.94	9.15±4.57
PLA/10wt%	58.05	130.8	153.0	0.62	60.90±0.70	8.03±3.01

3.2. Thermal properties

For better understanding the effect of PMMA-co-EA on the properties of PLA, a DSC was applied to observe the transition temperatures of the blends. Fig. 4 and Table 3 show the second heating DSC curves and their corresponding values observed form the DSC thermal scans. Neat PLA showed a T_g jump at around 61 ^{o}C other single small crystallization and melting peaks were observed at 120.3 and 154.8 ^{o}C respectively. By using Eq. (1), X_c of neat PLA was estimated by around 2%, which confirmed its amorphous nature mainly derived from L-lactide. This limited the crystallization of PLA and restricted PLA in high temperature applications [4-5]. Slight shifts of T_g by 2-3 ^{o}C were observed when PMMA-co-EA was added at all composition due to active interaction between PLA and PMMA-co-EA chains. This could be an indication of partial miscibility of the two polymers [18]. The identical cold-crystallization behavior was found in all PLA and modified-PLA represented by single cold-crystallization peak, while peaks

were shifted to higher positions around 10-11 ^{o}C. The increment of T_c and the decrement of T_m related to the depression of the crystallization ability of modified-PLA [19], which could be confirmed by X_c reductions. Generally, the addition of macromolecules like PMMA-co-EA usually obstructs PLA chains to recrystallize. This behavior had been reported by many researchers when PLA was blended by acrylate rubber [2], PBAT [19], acrylic core-shell rubber [1] and poly(butylene succinate-b-ethylene succinate) (PBSES) [20]. HDT values were varied in a narrow range from 1 to 3 ^{o}C or around 59-61 ^{o}C. This shortcoming still restricted the application of PLA in high temperature utilizations such as in microwave oven or hot water storage.
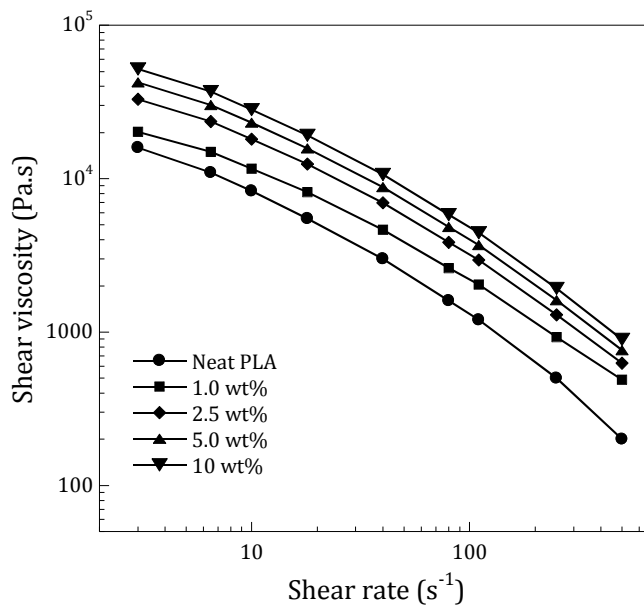

Fig. 5. Shear viscosity of PLA and PLA/PMMA-co-EA blends at 180°C.

3.3. Rheological properties

Relationship between the shear viscosity and the shear rate was graphically presented in Fig. 5. Under shear force, all of the blends showed a shear thinning character due to the decrement of shear viscosity. It was believed that the relaxation of PLA chains occurred under different shear deformation [10-11]. Blending PMMA-co-EA to PLA induced higher shear viscosity than neat PLA at all compositions. This related to the decrement of free volume due to the flow restriction. Maximum shear viscosity was observed when PMMA-co-EA was added at 10 wt%. In Table 3, the MFI of PLA decreased with increasing PMMA-co-EA concentration. This was due to the fact that PMMA-co-EA molecules could penetrate in PLA matrix and restricted the flow under melting stage. In the extrusion blow molding process, PLA melt required to be able to maintain certain elongational deformation. Thus PMMA-co-EA seems to be an appropriate way of rheological modification.
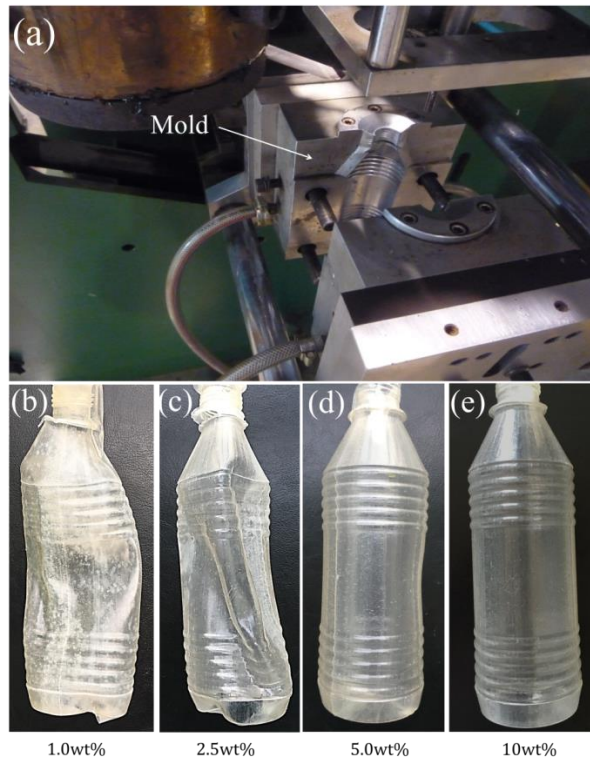
Fig. 6. Extrusion blow molding machine and blow molded products.

3.4. Extrusion blow molding

To fulfil the work, the PLA with 1.0, 2.5, 5.0 and 10 wt% PMMA-co-EA were blown by using an extrusion blow molding machine as illustrated in Fig. 6(a). With the identical processing condition, PLA with 1.0, 2.5 and 5.0 wt% PMMA-co-EA could not be fabricated as bottle, some flaws were observed. With 1.0 and 2.5 wt% PMMA-co-EA, Fig. 6(b) and 6(c) respectively, the bottles were not fully inflated the mold, due to curtaining or folding of the parison. This was the consequence of the high flow ability of PLA at low PMMA-co-EA contents. At 1.0 to 5.0 wt%, Fig. 6(b) to (d), flashes were observed at the bottle neck due to stock temperature and/or MFI were too high. In Fig. 6(e), PMMA-co-EA tended to give the best bottle blown product due to its proper flow properties. More than 10 wt%, the cost of raw materials will be increased.

4. Conclusions

In this paper, blow molded bottle was successfully fabricated by modifying PLA with PMMA-co-EA acrylic copolymer. With the presence of 10 wt% PMMA-co-EA, the blend was tougher with the increased elongation at break and impact resistance by 5 and 2 times respectively. All the modified PLA were found to have lower X_c due to the macromolecular incorporation. Rheological properties indicated that molten PLA was more viscous which reflected as the increased shear viscosity

and decreased MFI. PMMA-co-EA provided good bottle blown product at least 10 wt%. Less than this concentration, some defects were observed. More than this content, the cost of raw materials will be increased.

Acknowledgements

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