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Effect of PCL and compatibility contents on the morphology, crystallization and mechanical properties of PLA/PCL blends

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Abstract

This study focused on the effect of PCL on crystalline morphology, isothermally crystallization of PLA in PLA/PCL blends using POM on investigation. The blend with Pluronic used as a plasticizer was also studied. The blends were prepared by melt blending in an internal mixer. The contents of PCL incorporated were varied from 0-30 % by weight. The content of Pluronic used in this study was at 2.5, 5 and 7.5 phr. The blends were characterized for their morphology, crystallization and mechanical properties. Melt strength of the blends was also investigated. The morphology of the blends confirmed immiscibility of two polymer phases. Scanning electron microscope (SEM) of PLA/PCL blends indicated larger particle size of PCL dispersed in PLA with the increase of PCL contents. T_g of PLA in the blend could not be observed on Differential Scanning Calorimetry (DSC) traces. This was due to the overlapping with T_m of PCL. The presence of Pluronic in PLA/PCL blends resulted in T_ms shifting to slightly lower temperatures. The crystallinity of PLA was also decreased. The spherulitic growth of PLA in blends was followed by polarized optical microscope using isothermal condition at 141 °C. The spherulite structure was found affected by the presence of Pluronic hence effect on crystallization of PLA. Tensile properties of PLA/PCL blend were suffered with PCL content except for elongation at break which seems to be enhanced. It was found that the presence of pluronic in PLA/PCL blend increased ductility of the blends. At Plurunic of 2.5 phr and PCL content of 10-20 % by weight, tensile strength of these blends was increased. This was explained by the fine dispersed PCL particles facilitated orientation of PLA chain after proportional limit and hence increased tensile strength. With higher content both PCL and Pluronic, large PCL particle size was disadvantaged for tensile properties.

*Keywords:*Poly (lactic acid); Polycaprolactone; Crystallization; Polarized optical microscopy

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1. Introduction

Nowadays replacement petrochemical based polymers with bio-based polymers are interesting for packaging application. Many research efforts have been focused on aliphatic polyesters including polylactic acid and poly (ε-caprolactone) as the most important biodegradable materials. [1] Poly (lactic acid) (PLA) is one of the most popular biodegradable polymers which can be produced from renewable resources, known as linear aliphatic thermoplastic polyester. PLA is rigid and brittle below its glass transition temperature (T_g) which is in the range of 50-60 °C [2]. PLA has high tensile strength, rigidity and stiffness. [1-3]. Its high strength and biodegradability makes it an ideal candidate for packaging application. On the other hand, its brittleness limited their uses in many applications. The improvement for the brittle PLA to be better was studied in many researches. Huda M. S. et al. [4] reported that mechanical properties of the wood-fiber-reinforced PLA composites are suitable to be used in automotive and packaging industries. Also, few studies have used flexible polymers with PLA. PLA can be blended with flexible polymers such as poly (ε-caprolactone) (PCL), poly (buthylene succinate) (PBS), and poly (butylene succinate adipate) (PBSA) to achieve the flexibility and high elongation the brittleness of PLA and improves strain at break [1-6].It is well known that blending of polymer is the most cost-effective way to obtain material with required properties. The miscibility of two polymers can be determined by the Gibbs free energy of mixing by using the solubility parameter value of the two polymers [2]. Polycaprolactone (PCL) is semicrystallinealphatic polyester, flexible polymer and biodegradable but this one is obtained through petrochemical processes [3]. PCL has low glass transition and melting temperature (T_g = -50 ^{o}C, T_m = 60 ^{o}C) [5]. Blending of PCL with PLA can reduce brittle behavior of PLA.PLA blends with PCL have been report as phase-separate blend system [2-7]. Jen-Taut Yeh et al. [6] blended PLA with PCL by melt blending. They found that PLA and PCL form a partial miscible blend. Takeshi et al. [7] showed an increase of ultimate tensile strain of PLA when PCL was added to this blend system. Kamolrat et al. [8] used a block copolymer of poly (ethylene glycol) and poly (propylene glycol) as compatibilizer in PLA/PCL blends. SEM micrographs revealed that the PCL phase was better distributed and more miscible in the PLA matrix. The presence of compatibilizer increased strain at break.

The aim of this research is to improve the strength and ductility by incorporation PCL to PLA. The crystallinity of the blends is also aimed to be studied. The addition of PEG-PPG-PPE block copolymer is also added to investigat whether it to be a compatibilizer or plasticizer in the blends.

2. Materials and Methods

2.1. Materials

Poly (lactic acid) (PLA) grade 2003D, with melt flow index (MFI) of 6 g/10min (temperature 210^{o}C, pressing mass 2.16 kg), was purchased from Nature Works LLC. Poly (ε-caprolactone) (PCL) (CAPA^{TM} 6506 technology) with number-average molecular weight of 50,000 g/mol was purchased from Perstorp. The MFI, measured at 160 $^{\circ}$C, same pressing mass as for PLA, is in the range from 5.2 to 11.3 g/10min. Poly (ethylene glycol)-Poly (propylene glycol)–Poly (ethylene glycol) block copolymer (PEG-PPG-PEG), trade name Pluronic® L-81, was purchased from Sigma Aldrich with the number-average molecular weight of 2,800 g/mol.

2.2. Preparation of the PLA/PCL blends

PLA pellets and PCL powder were dried in hot air oven at 60 ^{o}C and 30 $^{\circ}$C respectively, for 12 hours before melt blending. The ration of PLA/PCL formulated for melt blending was 100/0, 90/10, 85/15, 80/20, 75/25 and 70/30by weight percentage. The blending was carried out by melt mixing using an internal mixer at 180 $^{\circ}$C with rotor speed of 50 rpm for 15 min.The PLA/PCL with Pluronic loading at 2.5, 5 and 5 phr was also processed under the same conditions.

After the melt mixing, PLA/PCL blends and PLA/PCL filled with Pluronic was compressed, using compression molding machine, at 160 $^{\circ}$C and 800 psi to obtain blend sheet with dimension of 15 mm x 18 mm x 0.7 mm.The blend sheet was cut into dumbbell shape (dog-bone), according to the ASTM D638 type 4A standard for tension testing, using laser cutter.

2.3. Charecterization

2.3.1 Crystallinity

Differential scanning calorimentry (DSC) wasused to examine crystallinity. The experiment was carried out with a MettlerTelado follow thermal cycles steps applied: (i) first heating step from 0 to 200 °C, (ii) cooling step from 200 to 0 °C and (iii) the second heating step from 0-200 °C. Heating and cooling scan were performed at 3 ^{o}C/min under a nitrogen atmosphere. Crystallinity of PLA phase in the blends taken from second heating scan was calculated using the following equation:

$$\chi_{c,PLA}(\%) = \frac{\Delta H_m}{w\Delta H_m^o} \times 1 \qquad (1)$$

where ΔI is the melting enthalpy of PLA crystal, and w is the weight fraction of PLA in the blend. A value of ΔI = 93 J/g was used as ΔH^0 of PLA [3].

2.3.2 Tensile testing

Mechanical properties of PLA/PCL blends and PLA/PCL filled with Pluronic blends were investigated using universal testing machine (Instron Corp., model 5969). Tensile testing was conducted on specimens using a crosshead speed of 50 mm/min. Young's modulus (E), tensile strength were determined as the mean value from at least ten specimens testing.

2.3.3 Morphological Investigation

Morphology of polymer blends was investigated from gold sputtered cryogenic fractured and tensile fractured surface using scanning electron microscope (SEM), Hitachi TM3030, at 15 kV.

Optical microscope (Optika B-600 MET-Nikon)attached with controlled heating/cooling stage was used to investigatespherulitic morphology of PLA/PCL blends and Pluronic filled PLA/PCL blend film. The blends film was firstly heated from room temperature to 200 °C at the heating rate of 10 °C/min, after 10 min holding the sample were then cooled to 141 °C at rate of 1 °C/min. This temperature was then hold for 90 min. Spherulite growth was recorded at this step every 30 min. Then cooling to 37 °C and hold for 10 min. At this temperature the spherulite was recorded every 5 min.

2.3.4 Melt Strength

The melt strength of Pluronic filled PLA/PCL blends was measured by using a Rosand RH7 Advance capillary Rheometer (Bohlin instrument) at 160 ^{o}C.A polymer melt strand extrudate was vertically pulled downwards from capillary die and took up by rotating rollers whose its velocity was increased at a constant acceleration rate. The tensile force in the strand was measured by the balancebeam and can be plotted as a function of time or velocity of the rollers. The force at which the polymers melt breaks is called the "melt strength". [9].

3. Results and Discussions

3.1 Morphology of polymer blends

SEM micrographs of the blends with various contents of PCL at 10, 15, 20, 25 and 30 % by weight are shown in Figure 1(a)-(e). It is clearly showed that the PLA/PCL blends were immiscible, in which the spherical droplets of PCL is distributed in the PLA matrix. However, the size of the droplets was increased with the content of PCL. Due to PCL having low T_m, i.e. 57.32 °C, at the mixing stage PCL should be totally melted and sheared to small droplet. At high PCL content the droplet couldcoalescence giving rise to larger droplet size [1]. When Pluronic is added, at 5 phr, into the PLA/PCL blendssize of the dispersed PCL particles tend to reduce. It could be seen that even though Pluronic was added the PLA and PCL are still not compatible. This indicates that Pluronic did not act as compatibilizer for this blend. In fact the presences of Pluronic may plasticize PCL as could be confirmed by the smaller size of the dispersed PCL particles.The Pluronic may also plasticize PLA as could be seen by more plastic deformationin the blend and also in PLA phase, see detail in section 3.3.

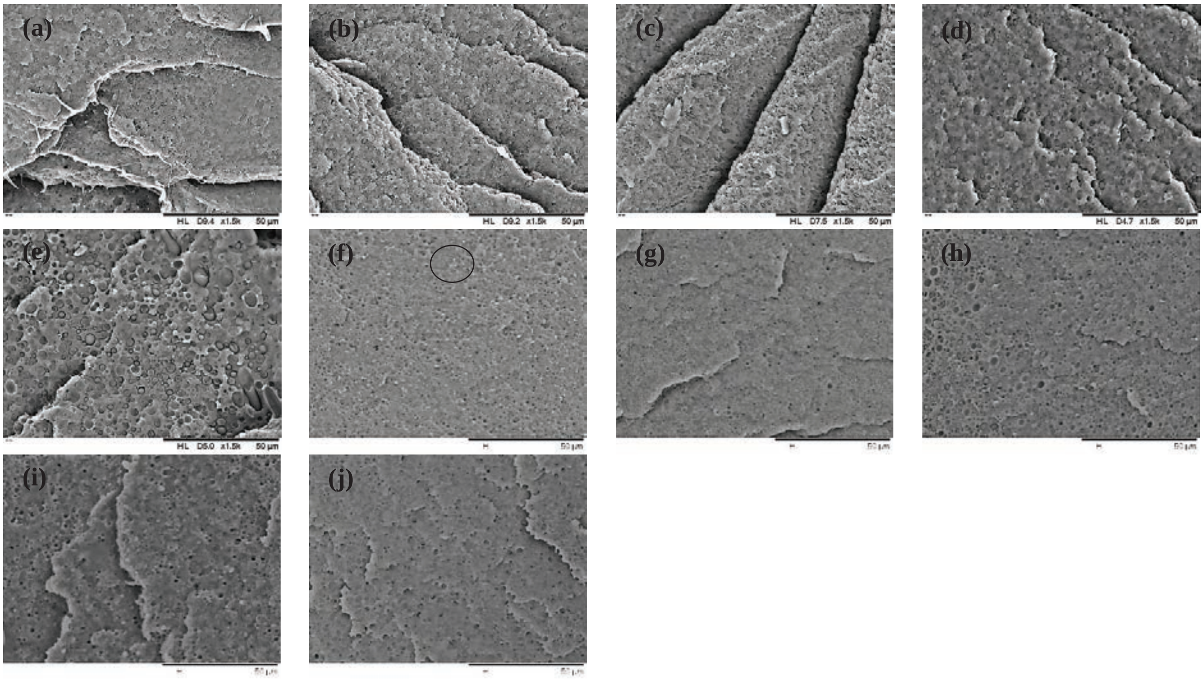

Fig.1. SEM images of blend of PLA/PCL with different compositions (a) 90/10, (b) 85/15, (c) 80/20, (d) 75/25, (e) 70/30, and PLA/PCL filled with 5phr of Pluronic(f) 90/10, (g) 85/15, (h) 80/20, (i) 75/25 and (j) 70/30

3.2Crystallization Behavior

Second heating DSC thermograms of neat PLA, neat PCL and PLA/PCL blends containing 0, 2.5, 5 and 7.5 phr of Pluronic are shown in Figure 2. The blends, at other PCL contents, without Pluronic were also investigated but were not shown here. The parameters were obtained from investigation are summarized in Table 1. Theoretically, glass transition temperature (T_g) of PLA is approximately occurred at 60.79 ^oC. In this blend system the T_g is very close to the melting temperature (T_m) of PCL (57.32 ^oC). Whereas the T_g of PCL, reported elsewhere [5], is approximately -61.5 ^oC. In this experiment we did not evaluate the T_g of PCL and hence no crystallization peak of PCL is noticed. As could be seen from the thermogram of all blends, T_g of PLA could not be detected due to the overlapping with T_m of PCL. Noticing T_{cc} and T_m of PLA in PLA/PCL without Pluronic blends compared to neat PLA, they tend to be unchanged. This could be due to the heat history was disappeared after the first heating scanned. The presence of Pluronic in PLA/PCL blends show the same tend as PLA/PCL blend without Pluronic. However, the T_{cc} was found to be lower than that of PLA/PCL blends without Pluronic. This could be the effect of Pluronic that act as plasticizer for PLA. In this case, T_g of PLA was unable to be detected owing to the overlapping with T_m of PCL. T_ms of PLA were also found to be slightly decreased with the presence of Pluronic. This could be due to the crystalline formed having different crystal structure from that in the previous system [10]. The crystallinity of all blends is determined using equation (1). As compared with the neat PLA, the percentage of crystallinity of PLA in PLA/PCL blends was decreased with the content of PCL. This could be due to the interruption of crystallization of PLA from PCL molecule during cold crystallization. As at this stage, PCL was already in melted stage [11]. The addition of Pluronic into the blends seems not to affect the percent crystallinity of PLA.

Table 1. DSC Results of the PLA/PCL blends with various amount of Pluronic From second scan of DSC curve

Content PCL (wt%)	**T_{cc} (^oC)**	**T_m (^oC)**	**ΔH_m (J/g)**	**PLA crystallinity (χ_c) (%)**
PLA/PCL blend				
0	98.86	145.99, 156.23	37.68	40.52
10	99.46	146.10, 155.96	27.76	33.17
14	97.76	145.68, 155.91	25.75	32.57
20	99.35	146.17, 155.96	28.20	37.90
25	98.45	145.70, 155.91	18.34	26.29
30	99.90	146.40, 156.16	23.18	35.61
PLA/PCL/Pluronic 2.5 phr				
10	93.16	143.61, 155.06	29.04	34.70
15	95.26	144.29, 155.18	26.37	33.36
20	96.51	144.75, 155.00	23.29	31.30
25	97.11	144.95, 155.20	22.48	32.23
30	96.61	144.85, 155.20	21.11	32.43
PLA/PCL/Pluronic 5 phr				
10	96.96	144.15, 154.00	29.40	35.13
15	95.00	143.95, 154.60	26.77	33.86
20	95.50	144.00, 154.51	23.48	31.56
25	94.15	143.65, 154.45	22.22	31.86
30	95.65	144.05, 154.31	19.94	30.63
PLA/PCL/Pluronic 7.5 phr				
10	94.87	144.21, 154.98	23.92	28.58
15	94.05	143.26, 154.30	24.8	31.37
20	95.00	143.90, 154.63	24.89	33.45
25	95.00	143.96, 154.71	23.23	33.30
30	93.50	143.32, 154.44	19.08	29.31

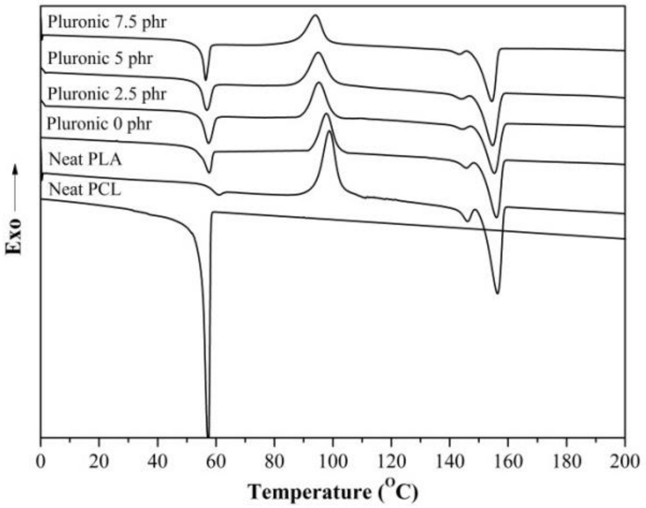

Fig.2. Second heating run DSC thermograms of PLA, PCL, and PLA/PCL 85/15 blends

containing 0, 2.5, 5, and 7.5 phr of Pluronic

3.3Mechanical Properties

Figure 3 shows the stress-strain curve of neat PLA and PLA/PCL 80/20 blends containing 0, 2.5, 5 and 7.5 phr of Pluronic. The strain at break of neat PLA and neat PCL is approximately 3.9 and 1200%, respectively. Also, The presence of PCL in PLA matrix resulting in the increasing of strain at break with PCL contents. But the strain at break tend to be decreased again after 15 % of PCL content. This report exhibited only PLA/PCL ratio of 80/20 where the elongation at break of the blend was turned to be suffered by 20 % PCL (4.6%). It was clearly showed that the addition of Pluronic prolonged strain at break of the blends from 4.6 to 43.4, 78.7 and 85.7 % strain when Pluronic added at 2.5, 5 and 7.5 phr, respectively. The percentage of strain at break increment was 843.48, 1610.87 and 1763.04% according to the Pluronic contents. This again confirmed the plasticizationeffect of Pluronic on PLA and PCL. The plasticization effect has occurred also evidenced by SEM micrographs shown in Fig. 5.

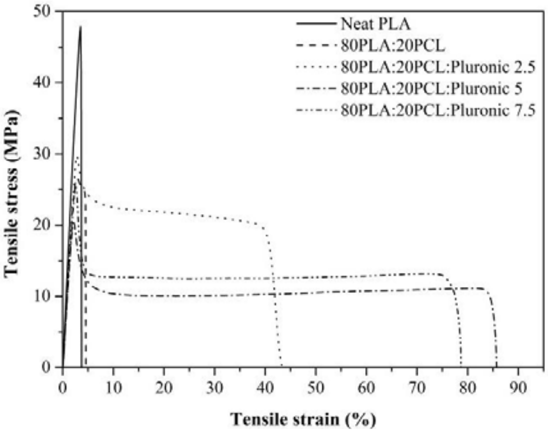

Fig. 3. Stress-Strain curve of PLA/PCL blends containing 0, 2.5, 5 and 7 phr of Pluronic

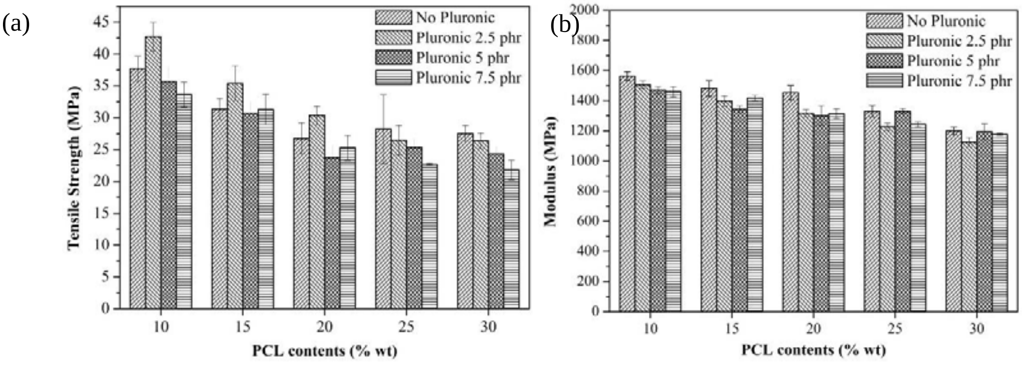

Fig. 4. Tensile properties of PLA/PCL blends containing 0, 10, 15, 20, 25 and 30 wt% of PCL and PLA/PCL blends with Pluronic loading 0, 2.5, 5 and 7.5 phr (a) Tensile strength at break (b) Modulus

The tensile strength at break of neat PLA and neat PCL were 52.9 MPa and 28 MPa, respectively. The addition of PCL in PLA matrix lead to the decreased in tensile strength including tensile strength at break of PLA/PCL blends.The results are shown in Fig. 4 (a). The PLA/PCL blends with Pluronic also showed the decreased in their tensile strength. This was not the case for PCL contents at 10-20 wt% where 2.5 phrPluronic was added. The tensile strength tended to be improved, but still lower than that of neat PLA, whereas at higher Pluronic added, tensile strength was dropped again. SEM micrographs in Fig.5 (a)-(c) and (f)-(h) should be taken into account again. It was noticed that with Pluronic, PCL particles were found smaller. This could facilitate reorientation of PLA molecules under tension after proportional limit. Theoriented chain would responsible for tend tensile strength. At higher Pluronic contents, PCL particles seem to be larger and hence obstructed the chain orientation.

In the case of Modulus, the result in Fig.4 (b) shows the same tend as tensile strength namely the modulus of PLA/PCL blends decrease with PCL contents. Neat PLA and neat PCL have modulus of 1749.5 MPa and 217 MPa, respectively. The addition of PCL into PLA increased ductility of PLA up to 15 wt%. After these content PLA tend to brittle due to large PCL particles and the phase separation, seen by SEM micrographs in Fig.6. Addition of Pluronic to the blends gave rise to lower the modulus. This again resulted from the plasticization effect of Pluronic on PLA matrix.

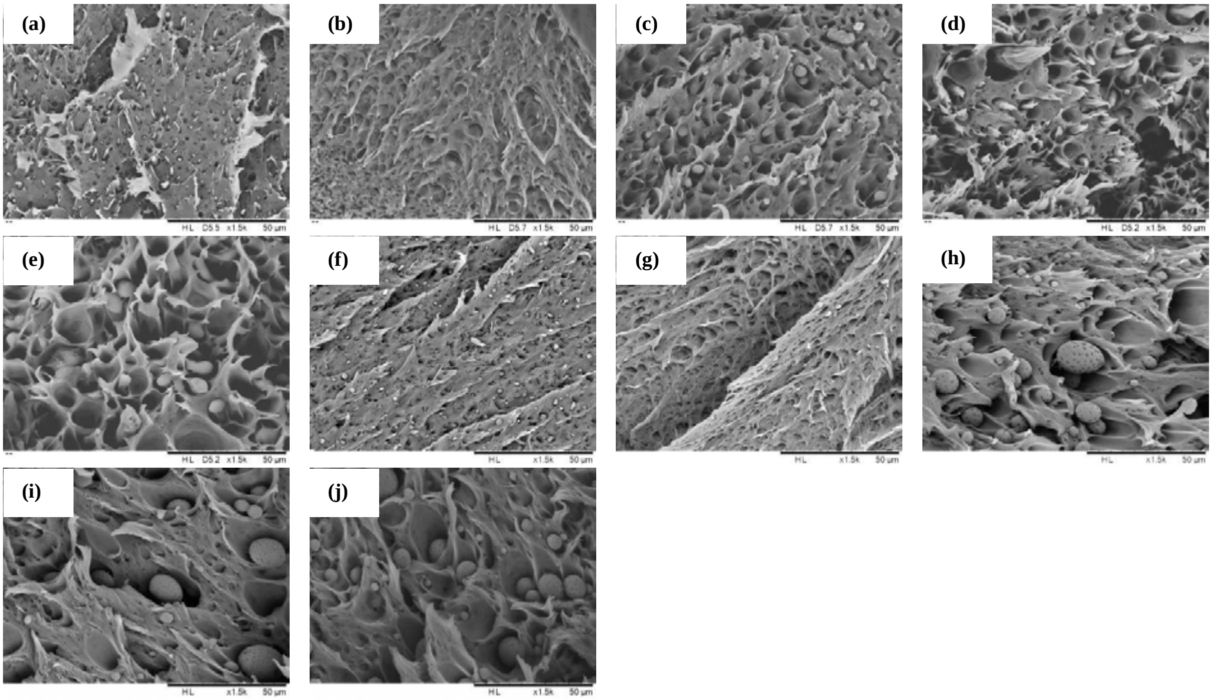

Fig.5. SEM images of fracture surface of PLA/PCL with different compositions (a) 90/10, (b) 85/15, (c) 80/20, (d) 75/25, (e) 70/30, and PLA/PCL/Pluronic composites (f) 90/10/5, (g) 85/15/5, (h) 80/20/5, (i) 75/25/5 and (j) 70/30/5

3.4 POM Analysis

Fig. 6 shows crystalline spherulite of PLA/PCL 85/15 and 85PLA/15PCL with Pluronic 5 phr. obtained from POM at 141 ^{o}C growth at 0, 30 and 90 min. The crystalline at 127 ^{o}C and 37 ^{o}C of both blends are also shown. In case of 85/15 blends without Pluronic, the spherulite of PLA at 141 °C are started to formed and its sizes are systematically increases with increasing time until at 127 °C. At 37 ^{o}C PCL crystalline was observed and the bulk blend consists of a large number of small spherulites of PCL including PLA spherulite. It can be observed that spherulites develop with extinction bands, a phenomenon also observed in other polymers which is attributed to the twisting of lamellae. [5]. The addition of Pluronic into the blend caused PLA to start its crystallization earlier, this agree well with the T_{cc}obtained from DSC. The droplet of PCL could also be noticed very clear in the micrographs. As can be noticed the spherulite radius of PLA is larger than the system without Pluronic. It can be notice carefully, the small particles appeared at the center of PLA spherulite which could be PCL particles. Also the characteristic of lamellae fibrill was slightly different from blend without Pluronic. This could be due to the twisting of lamellae [5] and resulted in differing crystalline structure. This results confirmed by the Tm present in DSC result.

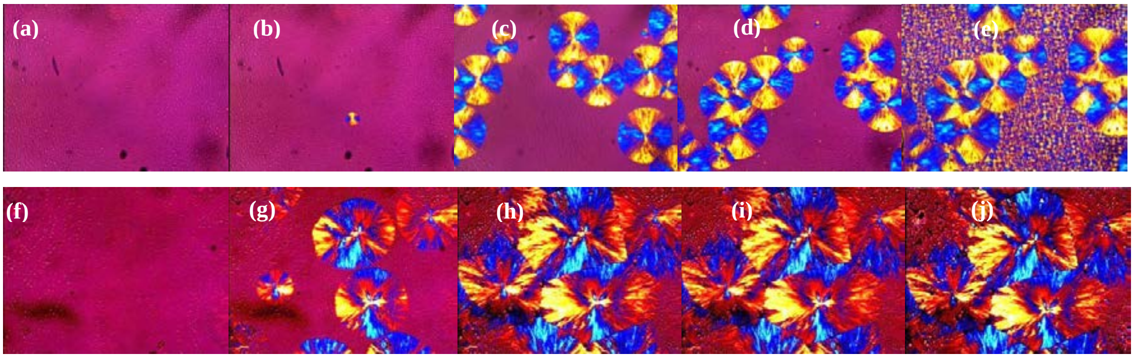

Fig. 6.Spherulitic growth in 85PLA/15PCL blends (a-e) and 85PLA:15PCL with Pluronic 5 phr blends (f-j) crystallined at (a) and (f) 141 ^{o}C; 0 min, (b) and (g) 141 ^{o}C; 30 min, (c) and (h) 141 ^{o}C; 90 min, (d) and (i) 127 ^{o}C and (e) and (j) 37 ^{o}C

3.5 Melt strength

Melt strength is a measurement of how strong a plastic is when it is in a molten state. A study of the variation of the melt strength of neat PLA and PLA/PCL blend filled with Pluronic 5 phr.The content of PCL at 10, 15 and 20 wt% added into PLA were carried out. It was found that melt strength of neat PLA is approximately 0.05 N. The addition of 10 % PCL into PLA gave rise to the slightly increased in melt strength. After this content the melt strength tended to be decreased. However the changed seem to be insignificant.

Drawability of the blend, shown in Fig.7 is considered. The results show that the addition of PCL into PLA increased drawability of polymer extrudate up to 15 wt% of PCL content. At high content of PCL, i.e. 20w%, the draw ability was decreased. This could be due to the large particle size of PCL and phase discontinuity.

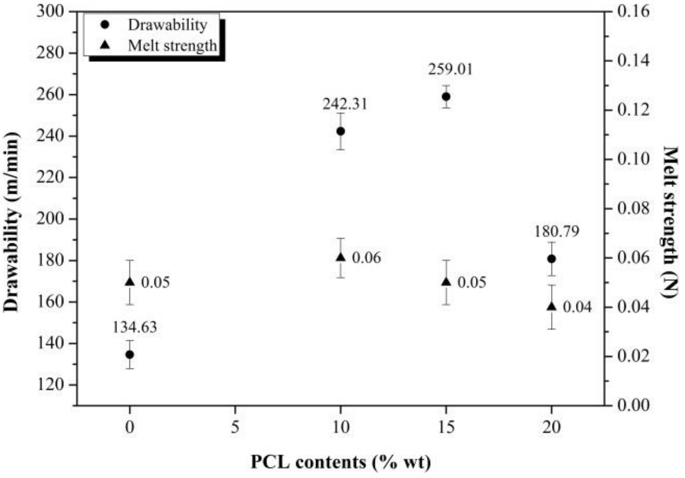

Fig. 7. Drawability (•) and Melt strength (▲) of Neat PLA and PLA/PCL/Pluronic 5 phr blends containing 10, 15 and 20 wt% of PCL at 160 ^{o}C

4. Conclusions

- *The effect of PCL on PLA*

  Morphology: The PLA/PCL blend was found immisible. The PCL was dispersed as small droplets. The particles seem to be larger with the content of PCL.

  Crytallization and Crystallinity: The addition of PCL into PLA decreased crystallinity of PLA whereas T_{cc}, T_ms seem to be unchanged.

  Mechanical properties: Addition of PCL into PLA suffered modulus, tensile strength of the blends. AtPCL content higher than 15 % by weight elongation at break was decreased due to the large particles size of PCL dispersed phase.

- *The effect of Pluronic on PLA/PCL blend*
  Morphology: The addition of Pluronic to PLA/PCL at 90/10, 85/15 led to smaller size of PCL dispersed phase. At high content i.e. 20-30 % by weight of PCL, PCL dispersed phase became larger. The addition of Pluronic would act as plasticizer for PLA. The PLA phase tends to show plastic deformation.
  Crytallization and Crystallinity: The crystallization of PLA was interfered with Pluronic and PCL as shown from POM. The twisting of lamellae seemed to appear in the blend system with Pluronic, This resulted in lowering in T_{cc} and T_ms. The crystallinity would seem to be slightly changed.
  Mechanical properties: The blend systems generally show inferior in modulus and tensile strength. But at the content of 2.5 phr of Pluronic added, tensile strength was being increased. This could be by the finely dispersed PCL particles and hence facilitated orientation of PLA chain after proportional limit. This caused the increase in tensile strength. The elongation at break of the blend seemed to be prolonged except for the content higher than 25 % by weight of PCL. This was by the plasticization effect of Pluronic on PLA and large particle size of PCL.
  Melt strength and draw ability: Although melt strength of system was seemed not to be affected, the drawability of the blend appeared to be facilitated by PCL at the presence of Pluronic as plasticizer.

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