PLA and two components silicon rubber blends aiming for frozen foods packaging applications

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ABSTRACT

Designing of PLA and two components silicone rubber blends was studies. Frozen food packaging application is the main ultimate aim. The statistical method using 2^3 DOE was conducted. The standard testing methods, in particular impact testing at sub-zero temperature, were performed. The preliminary blend formula comprised 1.0 phr of silane and polyester polyols, respectively, was initially resolved. Then, the optimize the silicone portion in the blends was determined. Blending formula using 8.0 phr of silicone with respect to PLA matrix gave rise to the overall satisfactory properties. 3. TETA was used as the silicone curing agent and reactively blended onto the ingredients. TETA at 0.4 phr, with respect to the silicone, enhanced the mechanical properties, especially flexibility and toughness, of the PLA/silicone blend. Exceeding the optimal TETA loading would cause the chain scission and also the dilution effects. Hence, marginal inferior properties of the blends were be experienced. The preliminary biodegradability investigation found that the PLA/silicone blend initially triggered at the second week. Its degradation rate was likely to be faster than neat PLA.

Introduction

Eco-friendly packaging especially with bio-plastics are the future for food packaging. [24,2]. PLA is eco-friendly, biodegradable, recyclable, and compostable. Nevertheless, the common drawback property is the brittleness in nature. It has less than 10% elongation at break. The improvement of mechanical brittleness can be done by polymer blending technologies [16,21]. Toughened poly(lactic acid) (PLA) by 5 wt% of a poly(caprolactone) (PCL) diol and triol based polyurethane (PU) network found that a maximum toughness of PLA can be achieved by introducing 5 wt% of a properly crosslinked polyurethane network [29]. The mechanical, morphological and thermal properties of PLA and LLDPE toughened PLA nanocomposites were investigated. The Young's and flexural modulus improved with increasing content of nanoparticle even at low content [7]. The improvement of the flexibility and strength of PLA blended with urethane polymer were reported. The elongation at break of the blends increased by 20 times in comparison with neat PLA. Impact resistance was also improved [10]. Melt blending of ethylene/acrylate copolymer, as impact modifier, and PLA showed the decreasing in tensile strength and modulus with increasing the impact modifier content.

However, the ductility and elongation at break was significantly increased. The relatively low temperature obtained for the PLA blends renders the ethylene/acrylate [1]. PLA blend with poly(-caprolactone) (PCL) in the presence of dicumyl peroxide (DCP) was studied. The samples at low DCP contents show yield point and ductile behavior under tensile test. The impact strength of the optimum composition was 2.5 times superior to neat PLA [23].

For works on PLA blended with rubbers to improve mechanical property was recently seen in many publications. PLA/NR and PLA/ENR blends were among the most popular ones [9,20,30,22,19]. The increasing in the tensile elongation up to 200% and superior in the impact strength were observed by blending 10–20 wt% of rubber with PLA. However, there has been no reported on the impact enhancement at sub-zero temperature by blending PLA with those rubbers.

Moreover, the research works on blending of silicone based rubber were mainly found only on the rubber blending. The molecular level and morphological characteristic of the blends were emphasized. The advantages on the thermal degradation and electrical resistivity improvement were reported [11,26,27]. There were seldom seen the publication on the blend of silicon based rubbers with thermoplastics.

The chain crosslinking is one of the methods to improve the properties of polymer. Thermal stability and mechanical properties of the crosslinked PLA via chemical treatment of the melt by

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adding small amounts of crosslinking agent triallyl isocyanurate (TAIC) and dicumyl peroxide (DCP) [28]. Silane-grafting water-crosslinking approach was employed to produce crosslinked poly (ʟ-lactide) (XPLLA) Thermal stability and mechanical properties, hydrolysis resistance was found to be significantly enhanced [13]. Not only in PLA, silane crosslinked wood polyethylene composites was also explored. The silane crosslinked composites by sauna incubation was significantly higher than for the non-crosslinked, no sauna incubation, composites. Improved adhesion between the wood and polyethylene phases was the reason for the improved toughness of the crosslinked composites [8]. Silane crosslink of ethylene octene copolymer (EOC) compound to improve the thermal and mechanical properties was published. The effects of filler surface characteristics on siloxane network structure developed and final properties of the crosslinked products were discussed. Crosslinked composites were able to withstand the high temperature environment of aging test [15].

From the above literatures reviewing, there are no scientific works concerning the toughness improvement of PLA compound or blending aiming for low temperature, especially at sub-zero level, applications especially for frozen food packaging. Sub-zero temperature toughness improvement of PLA aiming for the manufacturing of frozen food packaging was the ultimate goals for this research work. Silicones rubber, well known for retaining the flexibility at extreme low temperature, was blended with PLA. Systematic and stepwise exploration in the designing of PLA/Silicon blends using two-component silicone systems was explored.

Experimental

Materials

Poly(lactic acid) (PLA), 2002D, was purchased from Nature Works®. Two components silicone rubber system, SILASTIC® 3483, was available from Dow Corning Corporation. It was vulcanized at room temperature using triethylenetetramines (TETA) as curing agent. *gamma*-Aminopropyltriethoxysilane, Silquest A-1100, from Crompton Corporation was employed as coupling agent. High viscous liquid of polyester polyol, Rayelast A 8770, was employed as plasticizer. It was kindly supplied from IRPC Polyol Co., Ltd. All the chemicals used for compounding in the research were used as received.

Melt blending procedures

The schematic procedures of PLA/Silicone blends is illustrated in Fig. 1. PLA pellets were vacuum dries at 80 °C for at least 2 h. The calculated amounts of dried PLA, silicone mixed with TETA curing agent, silane, viscous polyester polyol and thermal/processing stabilizer were placed in the high speed mixer chamber and vigorously per-mixed for 1 min. The well premixed ingredients was melt blended on the co-rotating intermeshing twin screw extruders, Brabender Model PL2100 (Brabender®GmbH & Co. KG, Duisburg, Germany), having the screws diameter of 25 mm and L/D ratio of 20. The screws are consisted of 3 × 3 kneader blocks. Screw speed of 15 rpm and temperature profile at 140, 150, 160, 170, 180 °C, from feed to die head zones, were constantly and electronically controlled. The extrudate strand was allowed to cool down under the gentle cool air blowing. The blend stand was then pelletized into granule form.

The test specimen were manufacture using injection molding machine (CLF-80T; Chuan Lih Fa Machinery Works Co. Ltd., Taiwan). PLA/silicone blends pellet was vacuum dried at 80 °C for at least 2 h before molding. The barrel temperatures were set at 150, 160, 170, 180 °C from feed to nozzle zones and mold temper-
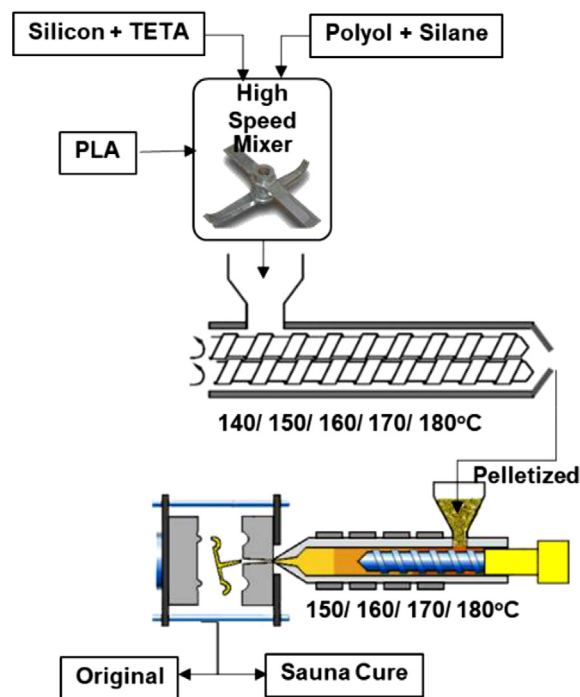

Fig. 1. The schematic diagram for PLA/silicone compounding.

ature was controlled at 30 °C. The holding and cooling times during the molding process were approx. 15 s and 30 s, respectively.

The molded specimens were equally divided into two sets of sample. The first set was allowed to anneal at room temperature for at least 24 h prior to conduct the testing. This sample was assigned as the "*original*" sample. Another set of sample was undergone incubation in the tight seal moisture saturated oven at 65 °C for 12 h. The method is known as sauna curing. It was performed to accelerate the completion of the crosslink via the silane-grated and water condensation reaction [13]. This set of injected piece was named as the "*sauna cured*" or "*cured*" sample in this publication.

Standard testing

The rheological properties of PLA/silicone blends by means of melt flow index (MFI) and melt viscosity were measured. MFI was tested in accordance with ASTM D1238 [6] using the Kayeness, Model 4004, melt flow indexer at 180 °C and 2.16 kg load. Shear viscosity of PLA/silicone blends at shear rate ranging from 10 to 1000 s^{-1} was obtained using a capillary rheometer from Kayeness, Model D 5052M, at the melting temperature of 180 °C. The compound pellet was dried in a vacuum oven at 80 °C for 2 h before testing. The zero shear viscosity (η_o) was calculated using Power law's model.

The tensile properties as described in ASTM D638 [4] was obtained using universal testing machine (Instron Model 5565) with 5 kN load cell. The cross head speed at 50 mm/min was electronically controlled. The dumbbell shaped specimens, type II, was employed. Izod impact strength, both notched and unnotched, was performed in accordance with and ASTM D256-10e1 [3] using the Atlas Impact Tester (Model BPI) were measured. The impact pendulum energy of 2.7 Joules was used for the notched impact testing. For the unnotched, the calibrated impact pendulum of 5.4 J was employed. The impact tests were conduct at room and sub-zero temperature, respectively. The sub-zero temperature testing was performed by immersion the sample in liquid nitrogen/methyl

alcohol mixture, −98 °C, for at least 5 min. Immediately, the sample was rapidly transferred onto the testing equipment and tested. By doing this, the material remain at temperature below 0 °C. Heat distortion temperature (HDT) was examined in accordance to ASTM D648-07 [5] using Atlas Testing Machine (Model HDV1) at 455 kPa load. Morphological observation on the notched impact specimens were conducted by scanning electron microscope (SEM) (JSM 6400).

The biodegradability observation of blends samples were conducted on the simulated landfill chamber filled with composted soil at 60 °C. The aerobic atmosphere was imitated by constantly feeding of oxygen gas or pumping the fresh air into the compost. The samples were removed to monitor the weight loss every 2 weeks and then placed back onto the same spot. The weight loss percentage was calculated by;

$$Weight\ loss\ (\%) = \left(\frac{W_0 - W_t}{W_0}\right) \times 100 \tag{1}$$

Where

w_o = Initial sample weight
w_t = Sample weight at given buried time (week)

Results and discussion

Design of experiment (DOE): effect of two components silicone(A), silane(B) and polyester polyol(C) contents

In this work, the basic the blending formula was initiated by adopting the design of experiment (DOE) method. Effect of two components silicone rubber(**A**), silane(**B**) coupling agent and polyester polyol(**C**) plasticizer contents was chosen as the DOE parameters. The statistical interpretation using tensile properties, impact strengths and HDT results, obtained from "*original*" and sauna "*cured*" of the blended samples were assigned as the main DOE responds. Table 1 shows high(+) and low(−) levels of each assigned parameters. Applying the 2^K rule, $2^3 = 8$ runs, the designed PLA/silicone blend formulation matrix was constructed in Table 2. The mixing batch size was based on 500 g of PLA. Table 3 summarizes the tested responds of the designed formula.

By applying the ANOVA method at 95% degree of confident ($\alpha = 0.05$) and using the Design Expert™ (Stat-Ease, Inc. USA) as the tool for analysis, the obtained regression models as the relations between the "*significant*" designed parameters and the assigned responds are concluded and demonstrated in Table 4. These equations could be statistically used to predict the properties of the PLA/silicone blend to the desired value. For example, the equation for notched impact strength of the original sample at room temperature is 3 + 0.43 (**A**). It means that amount of silicon rubber blended with PLA had the positive(+) significant effect on the notched impact of the blend sample without sauna curing tested at ambient temperature. If the maximum value of notched impact strength of PLA/silicone blend is required, high level of silicone (**A** > 3 phr) must be used for blending with PLA. The rest of the regression models can be explained and applied to resolve the relationship between the "*significant*" parameter and its properties.

According to the DEO conclusion found, it is generally seen that amount of silicone rubber(**A**), amount of polyester polyols(**C**) parameters and interaction between **AC** have the significant effect on most of the assigned properties responds for the original and cured samples. Starting with this DOE approach, the optimization of PLA/silicone formulation for low temperature applications can be further proceed. General speaking, the blend with good impact strength, at sub-zero temperature if possible, good flexibility by mean of high tensile elongation and relatively low HDT would be preliminary promising properties. Among those eight design ingredients, the run#5(+, −, −) formula not only show the outstanding low temperature impact strength but it also made from high amount of silicone(+**A**) and low amount of polyester polyols(−**C**) which have the significant effect on most properties. Therefore, the run#5 formula is chosen for further study on the ingredient refinement to optimize the property of PLA/silicone blend.

Optimization of the silicone rubber content on the PLA blends

Adopting the **Run#5** blend formula; low level(−) of silane content(**A**) at 1.0 phr, and low level(−) of polyol content(**C**) at 1.0 phr, the fine tuning of high level(+) of silicone contents was varied from 0 to 8.0 phr. Five blend formula are obtained as summarized in Table 5. They were assigned as Blend#0.0 to Blend#8.0, respectively. The batch size was based on 700 g of PLA. They were compounded on twin screw extrusion and injected into test specimen. The test results are summarized in Table 6. Samples from neat PLA and blow film grad LDPE, as typically used in frozen food packaging, were also conducted as and reported as referees.

One of the ultimate aims for this research work is the blown film product used for frozen food packaging. Consequently, the zero shear viscosities (η_o), as the basic rheological properties of the polymer melt, must be taken for consideration during the extrusion blown film. In this work, η_o is obtained from the power law model at melting temperature of 180 °C. According to the measured results, as expected, it is seen that the η_o of the PLA blends are shows the tendency to be lower with increasing the silicone content. It is due to the fact that silicone rubber had lower viscosity than the PLA melt. In comparison with neat PLA and LDPE, most of the blends, without sauna curing, have the η_o higher than the referee materials. On the sauna cured samples, the η_o is significantly lower than the original one. As expected, the macro crosslink would be formed via the moisture/silane induced condensation under sauna incubation [13,17]. The chain degradation would be occurred during the re-melt and shear the macro crosslinked blend on the capillary rheometer. Consequently, the η_o of the sauna cured blend would be lowered when compare with the original one. Also, the moisture traces in the cured blend, due to the prolong incubation in the moisture saturated oven, would not be ignored. Even though, all the samples were vacuum dried before testing. The tiny water residual would cause the chain hydrolysis during melting process. Then, the η_o of degraded polymer is lower. The exact trend, as seen on η_o, is also found for the melt flow index (MFI). MFI of the PLA blends show the tendency to be increased, lower in viscosity, with increasing the silicone content. At the given silicone content, the MFI of cured blend is higher, lower in

Table 1
The parameters and levels for DOE.

Design Parameters	High level (+)		Low level (−)	
(A) Silicone (phr*)	**+3.0**	**+2.0**	**−1.0**	**−0.5**
(B) Silane (phr*)	**+1.5**	**+1.0**	**−0.5**	**−0.2**
(C) Polyol (phr*)	**+5.0**	**+4.0**	**−2.0**	**−1.0**

* phr = part per hundred part of resin with respect to PLA

Table 2
Design matrix of PLA/silicone blends formula with k = 3.

Run#	PLA (g)	Silicone (A) (g) (phr)	Silane (B) (g) (phr)	Polyol (C) (g) (phr)
1#(−,−,−)	500	2.5 (−0.5)	2.5 (−0.5)	10 (−2.0)
2#(−,−,+)	500	5.0 (−1.0)	1.0 (−0.2)	25 (+5.0)
3#(−,+,−)	500	5.0 (−1.0)	7.5 (+1.5)	5 (−1.0)
4#(−,+,+)	500	2.5 (−0.5)	5.0 (+1.0)	20 (+4.0)
5#(+,−,−)	500	10.0 (+2.0)	1.0 (−0.2)	5 (−1.0)
6#(+,−,+)	500	15.0 (+3.0)	2.5 (−0.5)	25 (+5.0)
7#(+,+,−)	500	15.0 (+3.0)	5.0 (+1.0)	10 (−2.0)
8#(+,+,+)	500	10.0 (+2.0)	7.5 (+1.5)	20 (+4.0)

Table 3
Summary of the DOE responds obtained from each designed experiment.

Run#	Tensile Properties					
	Strength (MPa)		Elongation @ break (%)		Modulus (GPa)	
	Original	Cured	Original	Cured	Original	Cured
1#	43.91 ± 3.26	47.69 ± 5.83	4.49 ± 0.86	6.54 ± 1.12	2.49 ± 0.07	2.33 ± 0.07
2#	38.23 ± 2.18	41.04 ± 2.32	4.39 ± 1.56	8.77 ± 2.32	2.48 ± 0.08	2.21 ± 0.09
3#	38.99 ± 1.36	45.21 ± 2.23	6.05 ± 0.73	9.33 ± 3.35	2.52 ± 0.08	2.43 ± 0.08
4#	37.49 ± 0.87	43.10 ± 2.03	6.97 ± 2.04	8.19 ± 1.58	2.50 ± 0.06	2.23 ± 0.13
5#	34.28 ± 1.08	40.95 ± 2.04	7.56 ± 3.35	16.81 ± 0.78	2.52 ± 0.13	2.48 ± 0.13
6#	29.52 ± 3.77	38.60 ± 2.45	9.17 ± 2.23	12.45 ± 3.18	2.45 ± 0.05	2.31 ± 0.14
7#	31.63 ± 1.33	39.87 ± 1.30	12.92 ± 3.84	12.87 ± 3.24	2.53 ± 0.02	2.39 ± 0.07
8#	34.43 ± 1.82	42.27 ± 0.70	5.11 ± 3.46	9.97 ± 3.28	2.39 ± 0.18	2.38 ± 0.15

Run#	Impact Strength (kJ/m²)						HDT (°C)	
	Unnotched		Notched		Notched@Sub-Zero			
	Original	Cured	Original	Cured	Cured	Cured	Cured	Cured
1#	20.33 ± 3.03	22.24 ± 2.09	2.55 ± 0.21	3.25 ± 0.71	5.98 ± 0.68	5.37 ± 0.31	49.3 ± 0.6	59.3 ± 0.6
2#	21.54 ± 0.80	23.99 ± 2.91	3.07 ± 0.64	3.05 ± 0.23	3.68 ± 1.06	5.00 ± 0.36	48.1 ± 0.5	57.8 ± 1.6
3#	22.02 ± 3.32	23.22 ± 2.06	2.31 ± 0.16	2.96 ± 0.41	4.97 ± 0.81	6.45 ± 0.54	49.3 ± 0.6	57.7 ± 0.6
4#	26.02 ± 6.67	28.85 ± 3.75	2.38 ± 0.15	3.44 ± 0.26	4.90 ± 0.91	3.68 ± 0.43	47.9 ± 0.7	60.0 ± 1.0
5#	29.75 ± 3.19	32.78 ± 2.66	3.68 ± 0.85	6.34 ± 0.37	6.05 ± 0.60	6.40 ± 0.18	48.5 ± 0.5	57.9 ± 0.3
6#	26.02 ± 2.26	36.45 ± 6.85	2.81 ± 0.76	5.68 ± 0.29	6.07 ± 0.68	6.77 ± 0.35	47.3 ± 0.6	58.0 ± 0.4
7#	25.35 ± 2.87	30.35 ± 4.27	3.54 ± 0.59	5.93 ± 0.40	5.25 ± 0.93	7.38 ± 0.22	48.5 ± 0.4	60.3 ± 1.1
8#	20.64 ± 1.22	26.07 ± 2.49	3.69 ± 0.62	3.93 ± 0.12	5.58 ± 1.21	5.65 ± 0.59	47.8 ± 0.7	58.7 ± 2.3

Table 4
The regression models of the "*significant*" design parameters and the respond of the PLA/silicone blends.

DOE Responds	Regression Models	
	Original	Cured
Tensile Strength	36.06–3.60 (A)	No significant
Elongation @ Break	No significant	10.62 + 2.41 (A)
Tensile Modulus	2.49–30.69 (C) –22.99 (AC)	2.35–63.82 (C)
Notched Impact	3 + 0.43 (A)	4.32 + 1.15 (A)
Unnotched Impact	No significant	No significant
Notched Impact@Sub-Zero	No significant	No significant
HDT	48.35–0.30 (A)-0.56 (A)	No significant

viscosity, than the original one. The increasing in the MFI of the blends with increasing the silicone portion would probably be explained by the above fact that the silicone system used in this experiment is two components system. There was yet no curing used in these compound systems. Therefore, the added silicone rubber remained completely uncured and had low viscosity. Adding more uncured silicone into the blend ingredient, the viscosity of the material would become lower, higher in flow ability or MFI, at the higher rubber contents.

The thermal property by mean of HDT is also measured and recorded in Table 6. It is obviously noticed that HDT of the PLA/silicone blends without sauna curing are slowly declined with addition of silicone rubber. It is also seen that the HDT of the blends are lower than the neat PLA. Again, the lowering of HDT with

increasing the silicone content of the blends are foreseen. Because the silicone rubber has much lower in HDT than PLA. Surprisingly, after undergoing condensation reaction via the silance/moisture incubation of the blend samples, or sauna curing, their HDT are visibly hurdled close to 60 °C. The HDT of the sauna cured PLA/silicone blends are, more or less, shown the independency of the silicone contents. The domination of macro PLA chain crosslink resulted from the silane/water condensation reaction is owed for explanation. Typically, tighter packed amorphous chain, especially in network form, would have the higher heat resistance than the loosely chain arrangement. At this point, it is strongly emphasized that the macro crosslink, derived from silane/moisture condensation reaction, can be formed via the sauna incubation. After the curing process, the thermoset characteristic is commonly observed on the cured material.

For the mechanical properties by mean of tensile testing, it is observed that tensile strength of the original and cured sample are obviously decreased with increasing the silicone content. At any given silicone dosage, the strength of the blend is higher after undergoing sauna treatment. Meanwhile, the elongation at break is increased with increasing the silicone fraction. With the sauna incubation, the lower in the elongation at break is evidenced. The similar trend to the strength phenomena is also observed for the modulus. Regarding to the tensile properties reported, they reveal that the flexibility of the blends, especially for the sample without sauna curing, are increased upon the silicone loading. It means that the elastomeric behavior; low strength, high elongation and low modulus, of the blends is achieved. However, with macro network

Table 5
The designed formula with varying the two components silicone contents.

Blend	PLA (g)	Silicone (g) (**phr**)	Silane (g) (**phr**)	Polyol (g) (**phr**)
#0.0	700	0.0 (**0.0**)	7 (**1.0**)	7 (**1.0**)
#2.0	700	14.0 (**2.0**)	7 (**1.0**)	7 (**1.0**)
#4.0	700	28.0 (**4.0**)	7 (**1.0**)	7 (**1.0**)
#6.0	700	42.0 (**6.0**)	7 (**1.0**)	7 (**1.0**)
#8.0	700	56.0 (**8.0**)	7 (**1.0**)	7 (**1.0**)

Table 6
Summarize of test properties of the PLA/Silicone blends.

Sample	Silicone(phr)	η_o (Pa.s)		MFI (g/10 min)		HDT (°C)	
		Original	Cured	Original	Cured	Original	Cured
LDPE	–	3698	3631	2.86 ± 0.07	2.84 ± 0.05	36.6 ± 2.0	39.6 ± 1.6
PLA	–	4656	4320	1.41 ± 0.04	1.77 ± 0.02	51.7 ± 0.6	52.4 ± 0.7
#0.0	0.0	5495	3926	1.81 ± 0.02	2.84 ± 0.04	49.7 ± 0.7	58.0 ± 1.0
#2.0	2.0	5067	4169	1.91 ± 0.01	2.88 ± 0.04	49.5 ± 0.9	60.0 ± 2.0
#4.0	4.0	3855	2080	3.27 ± 0.04	4.74 ± 0.05	49.2 ± 0.7	60.2 ± 1.6
#6.0	6.0	4083	2388	3.07 ± 0.02	4.23 ± 0.05	47.5 ± 0.4	60.1 ± 0.8
#8.0	8.0	4882	2535	2.25 ± 0.05	3.10 ± 0.06	47.7 ± 0.6	60.0 ± 2.5

Sample	Silicone(phr)	Tensile Properties					
		Strength (MPa)		Elongation @break (%)		Modulus (GPa)	
		Original	Cured	Original	Cured	Original	Cured
LDPE		8.16 ± 0.43	8.43 ± 1.12	91.93 ± 2.26	91.28 ± 3.12	0.15 ± 1.22	0.14 ± 1.31
PLA		52.38 ± 0.93	59.48 ± 1.57	4.33 ± 0.26	4.94 ± 0.42	2.58 ± 1.07	2.67 ± 0.96
#0.0	0.0	46.11 ± 3.17	61.72 ± 1.71	3.77 ± 0.97	3.43 ± 0.14	2.42 ± 0.10	2.43 ± 0.12
#2.0	2.0	41.10 ± 4.65	41.66 ± 1.83	6.38 ± 1.56	4.30 ± 2.59	2.33 ± 0.04	2.49 ± 0.05
#4.0	4.0	31.38 ± 4.36	36.26 ± 1.16	7.23 ± 4.20	4.87 ± 0.88	2.34 ± 0.04	2.16 ± 0.10
#6.0	6.0	15.89 ± 7.79	35.34 ± 2.69	8.03 ± 2.76	5.28 ± 3.00	2.23 ± 0.10	2.18 ± 0.08
#8.0	8.0	15.61 ± 2.12	31.57 ± 1.60	11.4 ± 14.13	6.80 ± 3.19	2.04 ± 0.13	2.12 ± 0.13

Sample	Silicone(phr)	Impact Properties (kJ/m^2)				Impact Properties (kJ/m^2)@ Sub-Zero			
		Unnotched		Notched		Unnotched		Notched	
		Original	Cured	Original	Cured	Original	Cured	Original	Cured
LDPE	–	NB	NB	NB	NB	NB	NB	4.80 ± 1.34	3.60 ± 0.62
PLA	–	15.97 ± 2.35	21.15 ± 2.41	2.49 ± 0.48	3.45 ± 0.98	21.23 ± 1.34	22.15 ± 2.21	2.60 ± 0.62	3.20 ± 0.42
#0.0	0.0	20.54 ± 2.03	24.88 ± 3.39	2.84 ± 0.10	3.56 ± 0.31	23.96 ± 2.97	28.86 ± 2.20	3.88 ± 1.29	4.46 ± 0.89
#2.0	2.0	21.64 ± 1.87	29.29 ± 1.48	3.39 ± 0.25	6.08 ± 0.12	25.90 ± 3.47	26.55 ± 2.85	5.55 ± 1.03	4.70 ± 0.81
#4.0	4.0	23.07 ± 2.58	23.29 ± 3.59	2.58 ± 0.13	7.64 ± 0.34	20.78 ± 1.34	26.37 ± 1.59	4.65 ± 1.21	6.24 ± 0.80
#6.0	6.0	20.48 ± 1.70	24.97 ± 2.59	3.15 ± 0.32	9.14 ± 0.32	21.65 ± 1.88	35.44 ± 1.69	4.04 ± 1.03	6.54 ± 0.49
#8.0	8.0	22.23 ± 1.72	33.73 ± 0.48	7.68 ± 0.82	12.45 ± 0.26	23.79 ± 1.76	35.53 ± 1.06	6.40 ± 0.36	6.97 ± 0.20

forming via the silane/moisture reaction or sauna cured inhibits caused the elastomeric characteristic, more brittleness. This rubbery demonstrative with the silicone blending will also be evidenced in the impact testing results. Furthermore, in comparison with brittle neat PLA, more tougher and flexible properties of the PLA/silicone blends are apparently perceptible.

For notched and unnotched impact strengths conducted at room temperature shown in Table 6 reveal that the both notched and unnotched impact strength of the "*original*" samples are likely to improve with the fraction of silicone blends. Moreover, with the sauna treatment, the strengths are evidently enhanced on each given blend ratio. Once more, the both modes of impact strengths are clearly increased with increasing the silicone blending. These results endorse that the silicone rubber is effectively acted as the impact enhancer for the PLA blends. At this point, the impact strength value is recognizably higher than neat PLA. But, it is still much lower than the referee material, LDPE, which is commonly used in the frozen food packaging. The impact strength of LDPE, tested under the identical conditions, is non-breakable (NB). As emphasis earlier that one of the main ultimate goals of this work is to obtain the blend materials for utilizing in frozen food packaging applications. Therefore, the impact values tested at temperature far below 0 °C is avoidable. The notched and unnotched

impact strengths measured from the samples immersed in liquid nitrogen/methanol solution, approx. −98 °C, are also reported in Table 6. The similar outcome and trend to those tested at room temperature is observed. The impact strengths are noticeably increased with increasing the silicone loading. In addition, with the sauna treatment, the strengths of the "*cured*" sample is significantly higher than the original one. One underlined point at this stage of work is that the notched impact strength, tested under sub-zero condition, of PLA/silicone blends are very close to the notched impact strength of LDPE. This indication gain the confident that the manufacturing of PLA/silicone blend with better sub-zero temperature impact properties can be achieved and then applied as frozen food packaging applications.

The miscibility between disperse phase silicone rubber and PLA matrix is important not only mechanical property achievement but also have the significant concern on the clarity of the blends. Transparent or high translucent materials is prime desirable in food packaging industries. With naked eyes observation, the injected blend specimen is translucent. The clarity is diminished at high silicone blending. To verify the phase separation between PLA matrix and silicone disperse phase, the SEM technique was utilized. Figs. 2 (a) to 3(d) illustrate the SEM photographs of fractured notched impact specimens, at ambient testing, of the blends with silicone
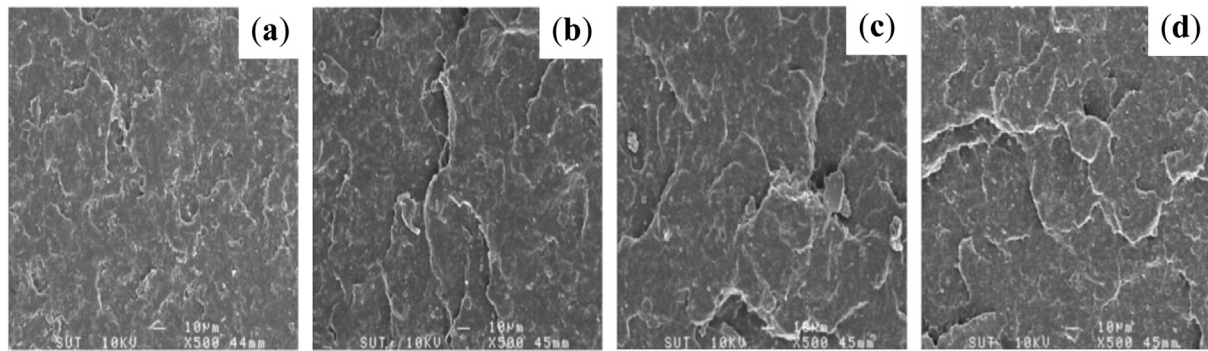
Fig. 2. SEM micrograph of PLA/silicone compound with silicone contents; (**a**) 4.0 phr (original), (**b**) 4.0 phr (cured), (**c**) 8.0 phr (original) and (**d**) 8.0 phr (cured), respectively at X500.
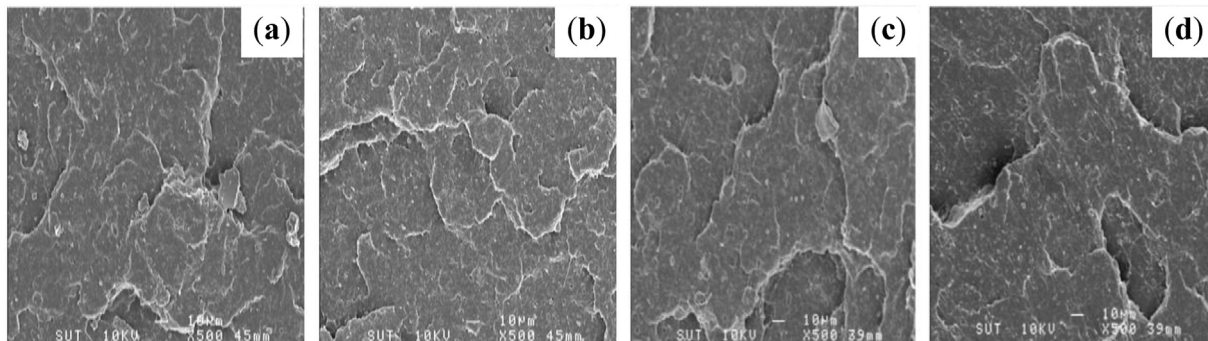

Fig. 3. SEM of the PLA blended with 8.0 phr of silicone rubber and using TETA as silicone curing agent at; (**a**) 0.0 phr (original), (**b**) 0.0 phr (cured), (**c**) 0.4 phr (original) and (**d**) 0.4 phr (cured), respectively, at X500.

loading at 4.0 phr and 8.0 phr before and after sauna curing, respectively. At 4.0 phr of silicone, very tiny drops of the added rubber is seen. When increasing the silicone content to 8.0 phr, the dispersed rubber drops are clearly visible. By closer observation on the given silicone dosing sample, the rougher fractured surface is apparently evidenced for the cured sample comparing with the original one. Moreover, the fractured surface roughness is more noticeable when the silicone content is increased. Accordingly, it manifests that the toughness by mean of impact strength is improved by the macro crosslinking due to the sauna treatment. Moreover, at high silicone content, with excessive rubber dispersion, the better impact strength is scarified.

Regarding to the above summarized results, the PLA/silicone blends having the silicone content varied from 0.0 to 8.0 phr were produced. The flexibility under load of the blends are increased with increasing the rubber fraction. Toughness by mean of impact strengths tested on both at room and sub-zero temperature was also improved with gradually increasing the rubber fraction. By introduction of the sauna treatment, it had the effective improvement on those properties. Reminding that silicone rubber employed in this work is two packs silicone system. So far, it was used without curing agent. In the following experiment, effect of adding TETA as the silicone curing agent will presented and discussed. The silicone blending content at 8.0 phr was selected.

Effect of TETA as curing agent for two component silicone system on the PLA/silicone blends

Above experiment, the two component silicone system was used without adding the rubber curing agent. In this section, tri-ethylenetetramines (TETA), typical curing agent for the two component silicone system, is explored. Taken the blend formula where PLA is blended with 8.0 phr of silicone as the optimal rubber fraction. Addition the TETA curing agent varied from 0.1 to 1.0 phr, in corresponding to of silicone, used were assigned. The total batch size and others ingredients in weight ratio were based on 800 g of PLA. Accordingly six blending formula were constructed as shown in Table 7. The melt blending processes were conducted in the identical fashion as described earlier. The test results measured on injected specimen, both original and sauna cured, of the blends are summarized in Table 8.

In Table 8, the zero shear viscosities (η_o) of the PLA blends before undergoing sauna treatment are obviously decreased with increasing the amount of TETA curing. At the given TETA dosing, the sauna curing of the blend sample is higher than the original one. Again, the macro network chain bonding through the silane/-moisture condensation reaction should be taken for explanation. Regarding to the amount of TETA as silicone rubber curing agent, the η_o result of the cured sample is also indicated the similar trend to those original blends. The η_o is undoubtedly manifested lower viscosity at high TETA loading. The dilution effect from the excessive amount of added TETA would be accounted for justification. Not only the shear viscosity of the PLA/cured silicone blends was analyzed in this work, also the flowability by mean of the melt flow index was also taken for consideration. The MFI of the blends with respect to the TETA content in Table 8 reveal that it is linearly increased with increasing the TETA content for both original and cured samples. However, in comparison between those samples, it is observed that the MFI of the cured is lower, higher viscosity, than the original one. As repeated mentioned, the macro crosslink must be responsible for this flow resistance behavior. The increasing in the MFI, or lowering in the viscosity, of the blends with increasing the TETA is probably explained by three contradict points. Adding TETA into the PLA/silicone blends, it acts as the silicone rubber curing agent. Silicone chains are extended though the curing reaction. Consequently, the viscosity of the PLA/silicone

Table 7

The blend formula with varying the TETA curing concentration.

PLA (g)	Silicone (g) (**phr**[*])	TETA (g) (**phr**[**])	Silane (g) (**phr**[*])	Polyol (g) (**phr**[*])
800	64.0 (**8.0**)	0.000 (**0.0**)	8 (**1.0**)	8 (**1.0**)
800	64.0 (**8.0**)	0.064 (**0.1**)	8 (**1.0**)	8 (**1.0**)
800	64.0 (**8.0**)	0.256 (**0.4**)	8 (**1.0**)	8 (**1.0**)
800	64.0 (**8.0**)	0.384 (**0.6**)	8 (**1.0**)	8 (**1.0**)
800	64.0 (**8.0**)	0.512 (**0.8**)	8 (**1.0**)	8 (**1.0**)
800	64.0 (**8.0**)	0.640 (**1.0**)	8 (**1.0**)	8 (**1.0**)

[*] phr corresponding to PLA.
[**] phr with respect to silicone rubber.

Table 8

Summarize the test results of PLA/silicone blends using TETA as silicone curing.

TETA (phr)	η_o viscosity (Pa.s)		MFI (g/10 min)		Tensile Properties					
					Strength (MPa)		Elongation@break (%)		Modulus (GPa)	
	Original	Cured	Original	Cured	Original	Cured	Original	Cured	Original	Cured
LDPE	3698	3630	2.86 ± 0.07	2.84 ± 0.05	8.16 ± 0.43	8.43 ± 1.12	91.93 ± 2.26	91.28 ± 3.12	0.15 ± 1.22	0.14 ± 1.31
PLA	4655	4320	1.41 ± 0.04	1.77 ± 0.02	52.38 ± 0.93	59.48 ± 1.57	4.33 ± 0.26	4.94 ± 0.42	2.58 ± 1.07	2.67 ± 0.96
0.0	3715	1905	2.25 ± 0.05	3.10 ± 0.06	15.61 ± 2.12	31.57 ± 1.60	11.4 ± 14.13	6.80 ± 3.19	2.04 ± 0.13	2.12 ± 0.13
0.1	1513	1676	3.98 ± 0.18	3.48 ± 0.08	23.63 ± 6.26	33.45 ± 2.19	13.59 ± 4.76	13.35 ± 7.62	2.24 ± 0.91	2.14 ± 1.09
0.4	676	1047	6.13 ± 0.22	4.87 ± 0.16	19.09 ± 6.41	30.89 ± 0.52	27.28 ± 5.61	21.16 ± 7.63	2.26 ± 0.59	2.22 ± 0.47
0.6	301	758	7.64 ± 0.33	6.54 ± 0.36	19.48 ± 5.18	29.04 ± 0.31	16.91 ± 3.86	8.76 ± 1.43	2.17 ± 0.37	2.01 ± 0.58
0.8	457	691	8.50 ± 0.47	7.02 ± 0.17	20.58 ± 8.80	28.09 ± 0.58	14.84 ± 4.01	15.24 ± 4.16	2.15 ± 0.21	2.00 ± 0.92
1.0	275	426	10.36 ± 1.06	9.70 ± 0.09	21.83 ± 9.29	28.53 ± 0.32	15.53 ± 12.02	13.93 ± 5.63	2.15 ± 0.28	2.08 ± 0.43

TETA (phr)	Impact Strength (kJ/m^2) @ RT				Impact Strength (kJ/m^2) @ Sub-Zero				HDT (°C)	
	Unnotched		Notched		Unnotched		Notched			
	Original	Cured	Original	Cured	Original	Cured	Original	Cured	Original	Cured
LDPE	NB	NB	NB	NB	NB	NB	4.80 ± 1.34	3.60 ± 0.62	36.6 ± 2.0	39.6 ± 1.6
PLA	15.97 ± 2.35	21.15 ± 2.41	2.49 ± 0.48	3.45 ± 0.98	21.23 ± 1.34	22.15 ± 2.21	2.60 ± 0.62	3.20 ± 0.42	51.7 ± 0.6	52.4 ± 0.7
0.0	22.23 ± 1.72	33.73 ± 0.48	7.68 ± 0.82	12.45 ± 0.26	23.79 ± 1.76	35.53 ± 1.06	6.40 ± 0.36	6.97 ± 0.20	47.7 ± 0.6	60.0 ± 2.5
0.1	19.38 ± 3.25	31.43 ± 2.23	6.24 ± 1.27	11.43 ± 0.68	29.46 ± 3.89	34.97 ± 0.68	6.50 ± 0.83	6.93 ± 0.54	42.7 ± 0.6	53.3 ± 1.2
0.4	37.74 ± 6.13	67.75 ± 2.05	7.77 ± 0.54	13.19 ± 0.32	35.40 ± 1.93	51.55 ± 4.23	6.63 ± 0.69	7.07 ± 0.46	44.1 ± 0.2	52.0 ± 1.0
0.6	25.63 ± 0.71	33.48 ± 1.29	7.53 ± 0.50	9.75 ± 0.27	34.67 ± 1.36	38.21 ± 5.45	5.82 ± 0.31	5.51 ± 0.19	43.4 ± 0.5	51.7 ± 1.2
0.8	31.48 ± 5.02	32.14 ± 3.87	8.45 ± 1.16	4.64 ± 1.50	36.52 ± 1.82	45.98 ± 8.41	5.89 ± 0.66	5.43 ± 0.76	43.2 ± 0.4	51.5 ± 0.5
1.0	27.41 ± 3.09	33.93 ± 4.65	5.42 ± 0.53	6.84 ± 0.12	29.76 ± 3.41	45.71 ± 8.49	6.87 ± 0.74	3.94 ± 0.69	42.5 ± 0.5	51.2 ± 1.1

blends would be increased, low in MFI. However, the excess added TETA would cause the aminolysis of PLA matrix chain [12]. Hence, high flowability, low viscosity, of the degraded PLA/silicone blend would be observed, especially at high TETA loading. The final fore-seen for the increasing in flowability with TETA addition is the dilution effect. The excess TETA would act as contaminated solvent for the blends. With good solubility, the blends containing low molecular weight TETA would demonstrate low viscosity, high MFI. Obeying from the rheological results found, the two later statements, chain aminolysis and dilution effect, would be the main suspects for the increasing in MFI with increasing the TETA addition. If the aminolysis, chain scission, is the main incident, the mechanical properties, especially toughness, of the blends would be abysmal with TETA loading. In fact, will be seen later on, the mechanical performances of the PLA/silicone blends do not deteriorate with the amine addition. With the dilution effect from the fractional amount of the excess TETA, it would act like "*plasticizer*". As the outcome, the blends would be more flexible and tough. Thus, from this point, it could preliminary state that the increasing in the flowability of the PLA/silicone blends is probably affected by the aminolysis and dilution or plasticizing effect of the excessive added TETA. This statement will be more clearly emphasis by the later mechanical properties discussion, especially impact toughness.

For the mechanical aspect with TETA addition, it is observed that tensile strength, tested on the original sample, has shown the tendency to be decreased with increasing the TETA content. It is also noticed that the tensile strength is clearly improved after sauna incubation. At the given blend formula, it is also seen that sauna incubation of the sample obviously increases the strength.

They are also shown the declining trend when further increasing of TETA. The similar diminishing trend with respect to the TETA addition is found for the modulus values. In addition, at the given amount of TETA, the modulus is fractionally decreased when the sample is treated in the sauna chamber. In case of elongation at break, the test values are likely to be increased with increasing the TETA content. As expected, the silane/moisture crosslink reaction does generally cause the lower in flexibility of the polymer blends. Low elongation is observed. In comparison between the PLA/silicone blends and neat PLA, it is noticeably seen that the strength of the PLA blend is much lower than neat PLA. Vice versa, the elongation of the blends are much higher than neat PLA. In general, it could say that the tensile properties of the PLA/silicone blends obtained in this study are close to the properties of LDPE.

According the tensile results established, it could point-out that by adding TETA, as silicone curing agent, on the PLA/silicone blend ingredient had enhanced the tensile flexibility, more rubbery, of the blend. Network chain formation, through the silane/moisture incubation, had introduced the thermosetting characteristic, less rubbery, on the blends. As stated above, the aminolysis/dilution effect resulted from the excessive amount of added TETA could be foreseen the rubbery like tensile properties of the PLA/silicone blends. This declaration will be further strengthen by the impact strength outcomes.

The notched and unnotched impact strengths, measured at room temperature, with respect to the TETA dosage are also reported in Table 8. With similar to previous discussions, the notched and unnotched impact strengths show the upright trend at 0.0–0.4 phr of TETA dosing. However, exceeding the TETA

beyond 0.4 phr, the declining tendency is possibly observed. Again, the impact strengths of the sample is superior by the sauna treatment. Furthermore, the strengths of sauna cured samples are noticeably increased when increasing the TETA up to 0.4 phr. Beyond this upper limit, the strengths become inferior. Moreover, it is seen that strengths of the PLA/silicone blends are superior to neat PLA, regardless to the TETA addition. However, they are far lower than the strengths of LDPE. No break (NB) is observed for LDPE at both modes of testing. Considering the test results of notched and unnotched impact strengths measured at sub-zero temperature condition, approx. −98 °C, regarding with the TETA contents are presented in Table 8. The similar trend to those tested at ambient temperature is perceived. The impact strengths are in upright trend when the amount of added TETA is increased up to 0.4 phr. Further increasing the TETA fraction had caused the downtrend in impact strengths. The maximum impact strengths, both notched and unnotched, are found at 0.4 phr TETA addition. With the impact strengths outcome, both at room and sub-zero temperature test conditions, it can emphasis that the optimal amount of TETA as silicone curing agent required for reactive melt blending of PLA/silicone rubber is in the range of 0.0–0.4 phr with respect to the amount of two component silicone rubber system. Dosing TETA beyond this optimal concentration will inferior the impact strengths. This remark is supported the early statement that the excess amount of silicone curing agent, TETA, would undergo aminolysis, chain scission, of PLA matrix chain and/or has dilution/plasticizing of the blends. As the result, the mechanical properties, especially toughness, of the manufactured blends would become inferior. Low in ductility and fracture toughness would be experienced. Taken the impact strengths found in this section as the key point criteria, it might say that the optimal amount of TETA as curing agent for "two component silicone rubber" is 0.4 phr. Adopting this ratio for manufacturing the PLA/silicone blend onto reactive melt twin screw extrusion will offer the polymer blend material with respectable mechanical flexibility. According to the impact testing results, it is additionally found that the impact strengths of the blends are not only exceptionally higher than neat PLA but, at sub-zero test condition, the notched impact strength is more superior to the film grade LDPE.

For the thermal property by mean of HDT as presented in Table 8, it is observed that HDT of the blends show the declining trend when the TETA content is increased for both measured on original and sauna cure samples. It is also notice that the sauna curing has caused the observable increase in the HDT. This observation reinforces the postulation that the occurrence of condensation reaction via the silane/moisture incubation the samples has given rise to macro chain crosslinking and hence elevated the HDT of the PLA/silicone blends. The descending trend of the HDT with increasing the TETA addition would be enlightened by aminolysis and dilution effects as previously manifested. Both effects are typically triggered the low service temperature, HDT, of polymeric materials, especially with low molecular diluents. Moreover, from the HDT testing outcome, there is no huge contrast in the HDT of the neat PLA and the blends regardless to TETA contents. However, the HDT of the PLA/silicone blends are significantly higher than LDPE. This could offer the advantage of the blends over LDPE in term of broader service temperature window during the filling process, if the blends are used to produce the food packaging.

The miscibility between dispersed silicone rubber and PLA matrix is important not only for the mechanical aspect but also its appearance, especially clarity of product in packaging industries. See-thru or partially visible, translucent, packaging is the prime desirable for biodegradable packaging. General visualization, the injected specimen, with the thickness approx. 3 mm, of the PLA/silicone blend is heavily translucent. However, the light transmission ability was evidenced. Of course, within the thinner sheet, the transmission becomes very promise for the packaging applications. However, for the sake of scientific purpose, the miscibility of PLA and silicone rubber had to be verified by the SEM technique. Fig. 3(a)–(d) are the SEM photographs taken from the fractured surface of the notched specimens. Samples, original and sauna cured, were blended using the TETA contents at 0.0 and 0.4 phr, respectively. When comparing between samples having 0.0 and 0.4 phr of TETA, there is no distinctive difference in term of the size and distribution of the silicone dispersed phase. Tiny drops of silicone rubber are randomly dispersed on the PLA matrix. With the carefully staring at the 0.4 phr TETA dosing samples, the fibril like traces on the fractured surface are witnessed. This evidence could enlighten that the silicone rubber chains are extended by adding the TETA curing agent. The rubbery behavior of silicone can be fully manifested its rubbery characteristic into the blend. Therefore, as evidences from the impact strength evaluation, it can effectively perform as the toughener in the blends.
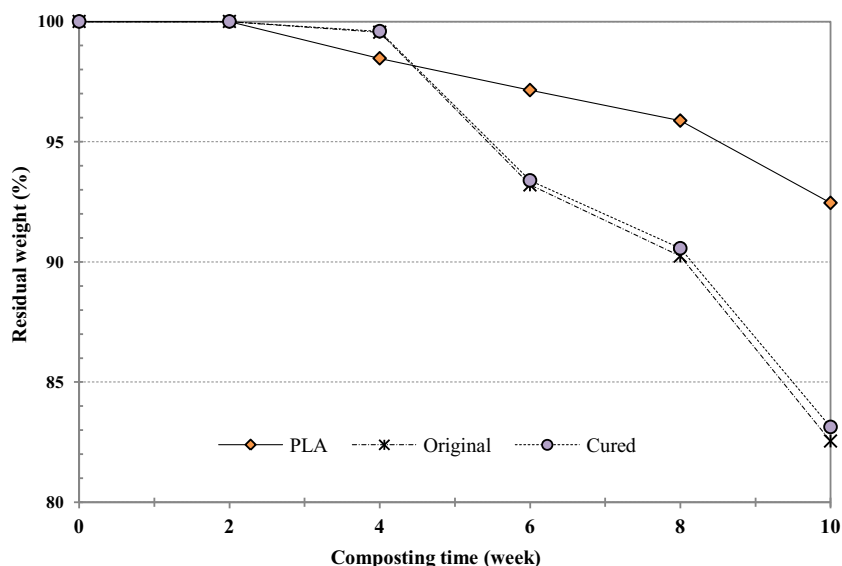

Fig. 4. Biodegradability investigation of neat PLA and PLA/silicone blend using 0.4 phr of TETA.

Elementary biodegradability investigation

One of the most important properties for conduction biodegradable polymers research is the biodegradability. Also, the ultimate aim of this study is to obtain the biodegradable polymer used for frozen food packaging. Therefore, it must be biodegraded under the landfill condition. Hence, biodegradability investigation is necessarily. The simulated landfill chamber, filled with composted material, at 60 °C under aerobic atmosphere was constructed. Fig. 4 shows the plot of the sample residual weigh against the composting times of the PLA/silicone blend and neat PLA injected specimen. The result indicates that neat PLA is slightly degraded for the first four weeks. After that, its biodegradability rate is visibly noticed. Within ten composting weeks, the PLA sample was disintegrated into small pieces where the residual weight measurement became impossible. Similarly, the injected PLA/silicone blend dumbbell test samples; having 8.0 phr of silicone, 1.0 phr of silane, 1.0 phr of polyol and 0.4 phr of TETA (with respect to silicone) both original and cured, illustrate that the degradation process is initially triggered at the second week of composting. After the fourth week forward, the degradation rate is sharply increased. Within ten weeks of the composting time, samples were completely and utterly disintegrated into the small pieces. At this point, the residual weight measurement was unmanageable. According to the biodegradability investigation observed in Fig. 4, it could validate that the degradability of PLA/silicone blend is faster than the neat PLA. It is well known and clarify that PLA is biodegradable polymer. It can be promptly biodegraded within 24 weeks. Obeying biodegradability investigation outcome from this study, it could pronounce that the PLA/silicone blend manufactured from this research work can undergo biodegradation in the similar manner as PLA. It is also discovered that the blend material can be biodegraded faster than the PLA.

Conclusions

1. The statistical study by mean of 2^3 DOE resolved the preliminary blend formula between PLA and two components silicone rubber. The optimal content of silane as coupling agent and polyester polyols as plasticizer at 1.0 phr was chosen, respectively. High level content of silicone rubber was recommended for mechanical enhancement.
2. The optimal content of two components silicone rubber system was concluded. Blending formula using 8.0 phr of silicone with respect to PLA matrix was found to manifest the overall satisfactory properties.
3. Adding TETA as the silicone curing agent into the blend ingredient had enhanced the mechanical properties, especially flexibility and toughness, of the PLA/silicone blend. The optimal TETA at 0.4 phr with respect to the silicone portion was recommended. Exceeding the optimal TETA concentration would cause the chain scission and the dilution effects. Hence, marginal inferior properties of the blends would be experienced.
4. The preliminary investigation on the biodegradability of the blend found that the PLA/silicone blend underwent biodegradation started within two weeks. It also evidenced that the degradation rate was likely faster than neat PLA.

Acknowledgments

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