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Optimization of the Effects of Thermoplastic Starch and Glycerol Concentration on Physicomechanical Properties of Polylactic acid/Thermoplastic Starch Blend by Response Surface Methodology

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Abstract

Polylactic acid (PLA)/Thermoplastic starch (TPS) blends as fully biodegradable materials have the potential of substituting petroleum-derived synthetic polymers for packaging applications and, especially producing disposable containers. In the present research the mentioned blends with compatibilizer were prepared by melt mixing method and the simultaneous effect of the factors of TPS weight percentage (CTPS) on the blend in the range of 10-50% and the glycerol weight percentage in its mixture with sorbitol (CGLY) in the range of 0-100% on tensile strength, impact strength and equilibrium moisture content of the blends was investigated by the response surface methodology. According to the obtained results, the blend with the optimum amounts of CTPS and CGLY of 34.9% and 28.7% respectively had the tensile strength, impact strength and equilibrium moisture content of 28 MPa, 25.5 J/m, and 14.3% respectively. The compatibilized PLA/TPS blend with the optimum amounts of CTPS and CGLY of 34.9% and 28.7% respectively, and the TPS phase containing 35 wt% of mixed plasticizer was prepared by a co-rotating twin screw extruder and its tensile strength, impact strength and equilibrium moisture content were measured. The relative deviation of the experimental data and the data predicted by the regression model for tensile strength, impact strength and equilibrium moisture content were 4.4%, 2.4% and 10.6% respectively.

Keywords: Optimization, Physicomechanical, Polylactic Acid, Response Surface, Thermoplastic Starch

Introductıon

The petroleum resources are finite and nonrenewable, therefore finding sustainable plastic substitutes especially for short-term packaging and disposable applications is being important increasingly. In packaging applications, agro-polymers derived from agro resources (like starch)

Extended Abstract

and synthetic biodegradable polymers like polylactic acid (PLA) may offer suitable alternatives to the conventional petrochemical polymers. Although products made from TPS exhibit good oxygen barrier properties (Dole *et al*., 2004), biodegradability (Iovino *et al*., 2008) and compostability (Lorcks, 1998), some deficiencies like strong water absorption (Teixeira *et al*., 2009), relatively poor mechanical properties and low thermal stability (Arboleda *et al*., 2015) limit their uses. PLA as an aliphatic biopolyester, is a transparent material when quenched from the melt and rigid with high tensile strength and low toughness. However, It is more expensive than conventional petroleum polymers for disposable or short-term applications and it degrades slowly in the environment over a period of several months to 2 years (Nampoothiri *et al*., 2010). The blending of TPS and PLA can enable tailoring the mechanical and physical properties and biodegradability of the stuffs made according to the required application and is a good way to balance the cost-effective issue and get a new material with good performances. But hydrophilic TPS, with plenty of hydroxyl groups and hydrophobic PLA, with hydroxyl and carboxyl end groups are thermodynamically immiscible due to the difference in chemical structure and behavior and present a poor interfacial adhesion (Wang *et al*., 2007). Maleic anhydride grafted PLA (PLA-g-MA) with degree of grafting of 1.2% was prepared by reaction extrusion method and was used in this research for compatibilizing (PLA)/(TPS) blends. Many of important and functional properties of the mentioned blend such as physical and mechanical properties can be affected by the two factors of CTPS and CGLY. Because in the previous studies the simultaneous effect of the two mentioned factors on physicomechanical properties of the blend have not been investigated so in the present study the simultaneous effect of the factors of CTPS in the range of 10-50% and CGLY in the range of 0-100% on tensile strength (TS), impact strength and equilibrium moisture content of the blend was investigated through experimental design performed by response surface methodology (RSM).

Material and methods

Natural wheat starch with a moisture content of 10% was purchased from the Iran's Momtaz starch company. The 2003D commercial grade polylactic acid with L-lactic acid content of 96% was obtained from America's Natureworks Corporation. Glycerol and Sorbitol as plasticizer for starch were prepared from the Merck company. High purity commercial grade magnesium nitrate for measuring the equilibrium moisture absorption content of samples was prepared from domestic suppliers. Wheat thermoplastic starch granules with 35 wt% of mixed plasticizers were obtained from the mixing of dry starch with mixture of glycerol and sorbitol and distilled water at a 61.75/33.25/5 dry starch/mixture of glycerol and sorbitol/distilled water weight ratio according to Table (1) by a co-rotating twin screw extruder, and then granulating. In order to prepare the blends formulations in accordance with Table (1), the dried components of the respective blend was melt mixed by the extruder and then turned into granules by the granulator.

Table 1. Formulations of PLA / TPS blends with wheat TPS phase prepared by glycerol, sorbitol or their mixtures

PLA-g-MA (phr)	CGLY (%)	CTPS (%)	Sample code	Test No.
4	50.0	10.0	CTPS10CGLY50	1
4	50.0	30.0	CTPS30CGLY50	2
4	100.0	30.0	CTPS30CGLY100	3
4	50.0	50.0	CTPS50CGLY50	4
4	14.6	15.9	CTPS15.9CGLY14.6	5
4	14.6	44.1	CTPS44.1CGLY14.6	6
4	50.0	30.0	CTPS30CGLY50	7
4	85.3	15.9	CTPS15.9CGLY85.3	8
4	50.0	30.0	CTPS30CGLY50	9
4	00.0	30.0	CTPS30CGLY0	10
4	58.3	44.1	CTPS44.1CGLY85.3	11

Each of the formulations was melted between the hot plates followed by cooling down to room temperature to obtain sheets with 200×200 mm sizes and different thicknesses for tensile, impact and moisture absorption tests. Tensile strength of the samples were measured at room temperature according to ASTM D638-02a (ASTM, 2002). Knoched izod impact strength of the samples were measured in accordance with ASTM D256-10e1 (ASTM, 2010). For equilibrium moisture content (EMC) determination, first each of samples (20×20×0.5 mm sizes) was placed in a sealed desiccator at 25 °C for 7 days over saturated salt solution of $Mg(NO_3)2$ having desired RH of 53% (Spiess & Wolf, 1983). Then the surface moisture of conditioned samples were gently removed by a tissue paper and then they were weighed by a precise microbalance before (w) and after drying at 105 °C for 24 h in a forced convection oven (w_0). The percentage of weight loss to the dry weight was calculated and was reported as EMC values of respective samples according to Eq. (1). For all tests 5 specimens of each sample were tested and their mean values were reported.

$$EMC = (\frac{W-W_0}{W_0}) \times 100 \qquad (1)$$

Results and discussion

The regression coefficients of linear effects, second degree effects and interactive linear effect of independent variables (CTPS and CGLY) on dependent variables (tensile strength, impact strength and equilibrium moisture content) and their meaningful (P values) derived from the fitting of the second-order regression model (Eq. 2) on experimental data were presented in Table (2).

$$Y_i = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^{\,2} + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \qquad (2)$$

Table 2. The regression coefficients of linear effects, second degree effects and interactive linear effect of independent variables on dependent variables and their meaningful

Coefficients symbol	Tensile strength		Impact strength		Equlibrium moisture content	
	Reg. Coeff.	*P*	Reg. Coeff.	*P*	Reg. Coeff.	*P*
β_0	31.0333	-	24.70	-	12.80	-
β_1	-9.5673	0.003	3.04	0.009	6.21	0.005
β_2	-0.9411	0.048	0.48	0.044	1.59	0.002
β_{11}	-0.0604	0.894	0.17	0.466	0.92	0.039
β_{22}	-0.1604	0.725	-0.21	0.379	0.52	0.179

Study of the simultaneous effect of CTPS and CGLY on the tensile strength of the blends

The results of Table (2) show that the linear effects of CTPS and CGLY on the tensile strength of the blends were significant at the 5% probability level (P<0.05), while their second degree effects and interactive linear effect on the tensile strength Were nonsignificant with a confidence of 95% (P>0.05). The values of the R-squared (R^2), Adjusted R-squared (R^2 (adj)) as well as the Lack of fit of the second-order regression model for tensile strength were 0.993, 0.986 and 0.268, respectively which indicated that the proposed second-order regression model predicted the effects of independent variables on tensile strength suitably. Considering the meaningful terms, this model for the tensile strength is expressed by Eq. (3).

$$Y_1 = 31.0333 - 9.5673X_1 - 0.9411X_2 \qquad (3)$$

The response surface graph of the simultaneous effect of CTPS and CGLY on the tensile strength is shown in Figure (1). It is seen that for any CGLY value, with increasing CTPS, the

tensile strength of the compatibilized blend decreased sharply. Considering that the wheat thermoplastic starch (containing 35 wt% of plasticizer) with a tensile strength of about 1 MPa, has a much greater flexibility than the poly-lactic acid with a tensile strength of about 60 MPa, it is logical that the increase of CTPS led to considerable reduction in tensile strength of the blend. In this context, similar results have been published by other researchers (Li & Huneault, 2011; Ebrahimi *et al*., 2016). Also, for any CTPS value (with the exception of blend No. 3), a slight decrease in the tensile strength of the blend was observed with the increase in CGLY. Regarding structural similarity and more compatibility of glycerol with wheat starch respect to sorbitol, glycerol plasticized wheat starches exhibit less tensile strength than sorbitol plasticized wheat starches (Yang *et al*., 2006; Sanyang *et al*., 2015). Therefore, increasing CGLY in the thermoplastic starch phase of the blends can reduce the tensile strength of the TPS phase and subsequently reduce its tensile strength.

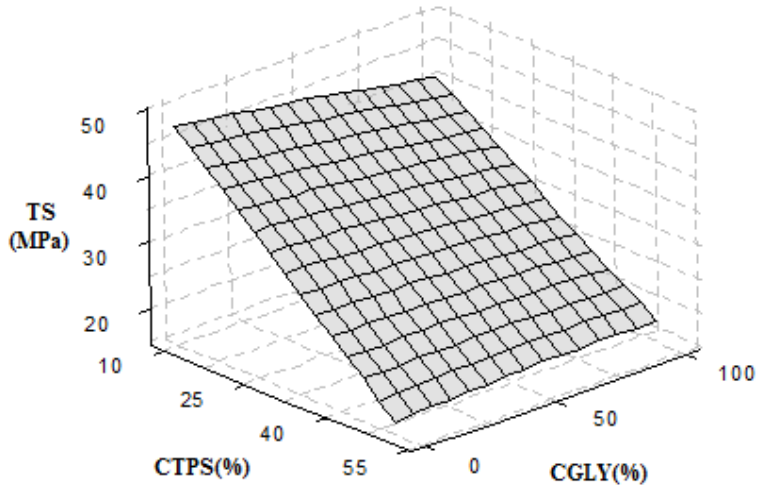

Figure 1. The response surface graph of the simultaneous effect of CTPS and CGLY on the tensile strength of the blends

Conclusion

Increasing both the two factors of CTPS and CGLY reduced the tensile strength of the blend although with different intensities but it led to increase in its impact strength and the equilibrium moisture absorption content although with different intensities. The optimum amounts for the independent variables of CTPS and CGLY were 34.9% and 28.7% respectively.

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Extended Abstract