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Material properties

Effect of phase inversion on the physical and mechanical properties of low density polyethylene/thermoplastic starch

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ABSTRACT

Blends of low density polyethylene (LDPE) and thermoplastic starch (TPS) containing low density polyethylene-grafted-maleic anhydride (LDPE-g-MA) as compatibilizer were prepared with various TPS contents. The effects of phase inversion on the morphological, static and dynamic mechanical and permeability properties of the blends were investigated. It was found that the morphology of the blend is matrix-droplet until the TPS content exceeds 75 wt%, when phase inversion occurs. The mechanical properties and glass transition temperature of the starch-rich phase decrease with increase of TPS content, and these reductions are more significant near the phase inversion point. The long term water absorption data of the blends were used to obtain the diffusion, solubility and permeability coefficients. The permeability properties of the blends change gradually at low TPS concentration, and the rate of these variations accelerates around the phase inversion point. Various models were used to predict these properties at different TPS contents.

1. Introduction

Disposal of enormous amounts of waste synthetic polymers pollutes the environment due to their high microbial resistance [1]. Raising this problem has led to growing attention to natural and biodegradable polymers such as starch from plants. Starch is a natural, renewable and inexpensive polymer, which can be decomposed with bacteria in the environments [2].

For processing starch it is necessary to destruct starch granules with addition of plasticizers (e.g. glycerol) under high temperature and extensive shear stress conditions, which results in the gel like material which is called thermoplastic starch (TPS) [3]. Since TPS is very moisture sensitive with poor mechanical properties [4,5], blending with other polymer is recommended [6,7]. The most studied polymer to be blended with TPS is polyethylene (PE), because of its widespread utilization for packaging and its strong resistance to biodegradation [8–12]. The first report of blending LDPE and LLDPE with TPS is that of St. Pieere et al. Their results showed that that the modulus of the blends decreased with increase of TPS content [13]. However, in the case of composites of starch granules and polyethylene, starch granules behave as a stiff filler and increase the modulus [14,15]. Because of high interfacial tension between starch and polyethylene [16], it is necessary to use a compatibilizer to increase the interfacial adhesion and enhance the mechanical properties of the blend [17,18]. Using polyethylene-co-vinyl alcohol (EVOH) [19], polyethylene-co-acrylic acid (EAA) [20], polyethylene-co-glycidyl methacrylate (PEGMA) [21] and polyethylene-g-maleic anhydride (PE-g-MA) [22] as compatibilizer has been reported. PE-g-MA is the most common compatibilizer and showed good efficiency in the case of PE/TPS blends. This improvement was attributed to the esterification reaction between maleic anhydride groups of PE-g-MA and hydroxyl groups of starch, and good interaction of its non-polar chain with the PE matrix [23]. Reactive

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compatibilization decreases the interfacial tension and leads to finer morphology [24]. Besides the interfacial tension, the morphological properties of the blends are affected by the rheological properties of the components, processing conditions and the component composition of the blends [25–27]. Rodriguez et al. showed that, by controlling the processing conditions, TPS and glycerol contents, a wide range of different morphologies such as spherical, fibrillar and even co-continuous can be formed [28]. The co-continuous morphology appears in a broad range, especially near the phase inversion point and usually at high concentrations of the minor phase [29,30]. There are many empirical and semi-empirical models for describing the phase inversion composition. Although most of these models used the viscosity ratio of the components to predict the phase inversion point, there are some models which consider other properties such as elasticity or damping factor to fit experimental results. Since the phase inversion phenomenon is not as yet fully understood, there is no general model predicting the phase inversion composition [31].

Although many studies have been done on PE/TPS blends, most of these works were performed at relatively low TPS content where the PE is matrix. At high TPS content, the morphology of the starch blends changes significantly and phase inversion occurs. Above the phase inversion concentration, the TPS as a dispersed phase turns into the matrix which results in poor mechanical properties and high sensitivity to moisture of the blend [32,33].

In the case of TPS blends with other polymers, the results showed that TPS degree of continuity is very high. Landreau et al. studied TPS and polyamide 11 compatibilized with carboxymethylcellulose, and found that the blend shows co-continuous morphology over a broad range, from 30 to 80 wt% of TPS, which is an indication of good compatibilization strategy [34]. In other work, Li et al. studied polycaprolactone (PCL) and TPS blends over the full range (from 0 to 100 wt%) of TPS. They showed that the blend has an asymmetric phase inversion region and shows a co-continuity range between 55 to 67 vol.% of TPS [35].

Significant changes in the morphology at the phase inversion point can affect various properties of the blends. The aim of this work is to study the evolution of the physical and mechanical properties as a function of TPS concentration for LDPE/LDPE-g-MA/TPS blends, especially at the phase inversion point. The reactive blending was performed from low to high TPS content and the changes in the morphology, tensile, dynamic-mechanical-thermal and permeability properties were tracked. In addition, prediction of these properties was attempted using models and comparisons made with the experimental results.

2. Experimental

2.1. Materials

Commercial LDPE resin, LDPE0200 (MFI = 2 g/10 min, density = 0.92 gr/cm^3), was obtained from Bandar Imam petrochemical company, Iran. Wheat starch, which consisted of 25 wt% amylose and 75 wt% amylopectin with moisture content less than 10 wt% (as measured by thermo gravimetric analysis), was obtained from Glucosan Company (Tehran, Iran). Analytical-grade Glycerol was purchased from Dr. Mujalli Co. (Tehran, Iran). LDPE-g-MA with 1.5 wt% maleic anhydride with a melt flow index of 2 g/10 min was provided by Grankin Co. (Tehran, Iran) and used as compatibilizer.

2.2. Sample preparation

Starch, LDPE and LDPE-g-MA were oven dried at 60 °C for 24 h. TPS was prepared by gelatinization of starch granules with 36 wt% of glycerol in an internal mixer (Haake, HBI System 90) at 130 °C for 2 min with 60 rpm rotor speed. The prepared TPS was then blended with LDPE and LDPE-g-MA at 130 °C for 5 min with 80 rpm rotor speed. The blend compositions are depicted in Table 1. For comparison, the neat LDPE and TPS were also processed under the same conditions. The samples were formed into the desired shapes by compression molding (Toyosiki press, Tokyo, Japan) at 160 °C and pressure of 25 MPa.

2.3. Morphological analysis

Before the test, rectangular bars were cryogenically fractured in liquid nitrogen. The samples were then etched at room temperature with 6 N HCl solution for 12 h to extract the TPS phase. The etched samples were washed with water and dried in an oven for 24 h. The morphologies of the blends were investigated by scanning electron microscopy (SEM) using a Vega Tescan microscope. The samples were coated with gold before the test. The size of the particles was analyzed using ImageJ software. For each sample, at least 200 particles were considered to characterize their morphological parameters. Because of the irregular shapes of the particles, it is necessary to quantify the particle diameter (d) using the area of each particle (A):

$$d = \left(\frac{4A}{\pi}\right)^{1/2} \tag{1}$$

The circularity ratio of the particles (C) was calculated as follows:

$$\text{Circularity ratio} = C = 4\pi\frac{area}{(perimeter)^2} \tag{2}$$

A circularity ratio of 1 means a perfect circular shape and zero implies an infinitely long and narrow form [36].

Table 1
Component composition of the samples.

Sample code	LDPE (wt%)	TPS (wt%)	TPS (vol%)[a]	LDPE-g-MA
LDPE	100	0	0	0
TPS	0	100	100	0
LTC20	75	20	15	5
LTC35	60	35	27	5
LTC60	35	60	51	5
LTC75	20	75	68	5

[a] The density of TPS was assumed 1.31 gr/cm^3 to calculate its volume composition [35].