Influence of modified nano silica particles on compatibility of linear low-density polyethylene/poly (lactic acid) blends

Maryam Hoseini and Ali Haghtalab

Department of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, 009821 Tehran, Iran

ABSTRACT

Effect of Modified silica nanoparticles as compatibilizer in immiscible linear lowdensity polyethylene/ poly (lactic acid) (LLDPE/PLA) blend have been studied. Silica surface was treated with hexadecyltrimethoxysilane agent to improve hydrophobicity properties of silica. Addition of modified silica into LLDPE/PLA blend have increased the complex viscosity and storage modulus. The good morphology was observed for the LLDPE/PLA/modified silica that indicate modified silica have improved the compatibility of blend and acted as compatibilizer.

INTRODUCTION

In recent years, excessive consumption nonbiodegradable plastic materials and increase of plastic wastes has become a serious and critical problem all over the world. The biodegradable polymers are expected to be an alternative for commodity synthetic polymer for solving this problem¹, . However, high cost of biodegradable polymer has limited its substitution with synthetic plastic. Thermoplastic polymers are blended with biodegradable polymer to overcome this limitation and prepare partially biodegradable polymer materials for specific end-uses^{3, 4}. Polyethylene (PE) is one of the most consumed non degradable polymers, and is mainly used in the packaging industry. It can be blended with biodegradable polymer for development of the biodegradable plastics. Among the biodegradable plastics, poly (lactic acid) most widely (PLA) is the used biodegradable polymer due to good mechanical properties, resistance to fats and oils, excellent transparency, and biodegradability. Thus, PLA may be a suitable candidate for blending with polyethylene^{5, 6}. Therefore, PE/PLA blend may be a suitable choice as an alternative to petrochemical polymer in the various applications especially packaging materials. PLA and PE usually form an immiscible blend due to the difference in their chemical structures and high interfacial tension. Therefore, to achieve useful products from PE/PLA blends requires to improve compatibility of PE/PLA blends. Several studies have been carried out to investigate the effect of the different compatibilizers on blends⁷⁻¹¹. immiscible PE/PLA Block copolymer (PE-b-PLLA) has been known as compatibilizer for PLLA/PE blends. The effects of glycidyl methacrylate (GMA)grafted poly (ethylene-octene) copolymer compatibilizer on (mPOE) as phase structure of PLA/LLDPE blends were studied¹⁰. Recently the use of nanoparticles for compatibilization of immiscible blends has attracted the attention of polymer scientist^{12,13}. Mechanical, thermal and morphological properties of poly (lactic acid) /linear low density polyethylene in the of organophilic modified presence montmorillonite (MMT) were studied¹⁴. The

enhancement of mechanical and thermal properties of PLA/LLDPE nanocomposites were observed by addition MMT platelets. Nano-silica particles have very high active surface areas with a variety of surface treatments from hydrophilic to hydrophobic, so that nano-silica particles are used as filler in various industrial applications to control rheological properties^{13, 15}. Sareeladdanon et al.¹⁶ were used rice husk silica as filler for improvement of mechanical properties of PLA and LLDPE. Jalali Dil et al.¹⁷ have examined localization of micro- and nanosilica particles in PLA/LLDPE by using thermodynamic and kinetic parameters. The results have shown that kinetic parameters had not significantly effects on the equilibrium localization of well dispersed spherical nanoparticles in a high interfacial tension polymer blend system. Commercial silica (SiO₂) and calcium carbonate (CaCO₃) nano-fillers as compatibilizers were used in immiscible PLA/LDPE blends¹³. The results have indicated that SiO2 filler was a better potential compatibilizer than CaCO₃ for a given PLA/ LDPE blend sample. Silica nanoparticles are hydrophilic due to the presence of a large number of Si–OH groups at the surface of the particles. Therefore, it is more difficult to disperse silica in hydrophobic matrix. In order to improve dispersion. the silica surface is usually modified with silane coupling agents¹⁸⁻²⁰. Replacement of the Hs from the Si-OH groups by the Si-R groups through the oxygen bonds produce hydrophobic silica surfaces^{18.} Two types of fumed silica (hydrophilic and hydrophobic) were used as filler in PP/PS blend²¹. It is found that hydrophilic silica tends to remain in the PS phase whereas hydrophobic silica is dispersed in the PP phase and at the PP/PS interface.

In this study, the effect of modified silica nanoparticles on rheology and morphology behavior of LLDPE/PLA blend have been investigated. In fact, the modified silica nanoparticles as compatibilizer were used for immiscible LLDPE/PLA blends. Hexadecyltrimethoxysilane agents were used for treatment of silica to improve the hydrophobicity properties of silica.

MATERIALS AND METHODS

Poly (lactic acid) grade 8052D, with a melt flow index of 14 g/10 min (210°C, 2.16 kg), was purchased from Nature Works. It contains 95.4% L lactide and 4.6 % D-content. Linear low density polyethylene (LLDPE) with a melt flow index of 0.9 g/10 min (190°C, 2.16 kg) was obtained from Amir Kabir Petrochemical Company, Iran. SiO₂ nanoparticles (AEROSIL 200) was supplied by Germany Degussa. The average particle size of SiO₂ was approximately between 20-35 nm with specific surface area of 200 m²/g. For treatment of silica surface particles, Hexadecyltrimethoxysilane was supplied by sigma Aldrich.

SAMPLE PREPRATION

The silica surface nanoparticles were treated with hexadecyltrimethoxysilane through alcohol-water media. At first step, an amount of silica nanoparticles was added to alcohol to prepare a uniform silica suspension using ultrasonicator. То performing silanization reaction, a proper amount of silane was mixed with the silica suspension by stirring for 24 h at room temperature. Then, the prepared mixture was placed in an oven at 110°C for 48 h to finish the silanization reaction. The final sample was centrifuged for three times to removing unreacted silanes. Finally, the modified silica was dried in an oven for 1 week.

Raw materials were dried for 24 h at 80°C in an oven to remove water and the other volatile components. Linear low density polyethylene/poly (lactic acid) (50/50) blend with various silica loading were prepared using a 40 cc internal batch mixer (Brabender, 50EHT) at 160 °C for 10 min and with a rotor speed of 60 rpm. Moreover, the LLDPE, PLA and SiO2 were pre-mixed and feed to mixer simultaneously. The prepared samples were molded into discs (2 mm thick, 25 mm diameter) by compression at 160 °C and 300 kPa using a laboratory press. These polymeric discs were used for the rheological measurements using a parallel-plates rheometer.

CHARACTRIZATION

The dynamic rheological behavior of various blend nanocomposites were investigated in the melt state through an oscillatory shear experiment using a parallel plate rheometer (Paar Physica UDS 200) with 25mm diameter and 1 mm gap at 160°C. Frequency sweep and amplitude sweep tests were performed for the blend nanocomposites samples. Linear viscoelastic region was determined using dynamic strain amplitude sweep test from 0.01 to 1000% and at angular frequency of 1 rad/s. The frequency sweep tests were carried out at the linear-viscoelastic region ($\gamma = 0.5\%$) in the range 0.01 to 628 rad/s.

The morphology behavior of the fracture surfaces was examined by SEM analysis (KYKY, EM3200, China) at an accelerating voltage of 26 kV. The samples were submerged in liquid nitrogen to preventing large deformations in the surface. Prior to examination SEM image, the fracture surfaces was coated with a thin layer of gold in an automatic sputter coater.

RESULTS AND DISCUSION

The rheological properties of polymers addition significantly change by of nanoparticles. The measurement of the viscoelastic properties of nanocomposites is necessary for optimization of their process viscoelastic Moreover, linear ability. behavior in the molten state is generally useful to study the structure of nanocomposites^{22.23}. Fig. 1 shows the storage (G') versus strain at $\omega = 1$ rad/s for the LLDPE/PLA (50/50) blend with the various wt. % of silica. The storage modulus has enhanced by increasing of the silica loading. It has been shown that the linear viscoelasticity region (Newtonian plateau) is specified at low strains and a non-linear behavior at high strains. The critical strain, in which the nonlinear behavior commences, reduces with increasing weight percent of nanoparticles. The decrease of storage modulus of nanocomposites at critical strain can be attributed to the breakdown of particle agglomerates since most polymer chains keep almost the equilibrium conformation under the critical strain of nanocomposites. The critical strain decreases from 0.63% to 0.1% LL/PLA (50/50) samples as weight fraction of silica increases from 0 to 8 wt.%. The nonlinear behavior in all samples is attributed to deformation of polymer chains and the destruction of the nanoparticles agglomerates.



Figure 1. The storage modulus (G') versus the shear strain for the LLDPE/PLA/SiO2 (50/50/SiO2) blends with various wt. % of modified silica nanoparticles.

The dependence of loss modulus on strain is shown in Fig. 2. The similar behavior was observed for loss modulus for the all samples. It can be observed the loss modulus enhances with increasing loading of silica nanoparticles.



Figure 2. The loss modulus (G'') versus the shear strain for the LLDPE/PLA/SiO2 (50/50/SiO2) blends with various wt. % of modified silica nanoparticles.

Figs. 3 and 4 show the storage modulus and complex viscosity of LLDPE/PLA (50/50) blends with the various weight percentages silica versus angular frequency at 160 °C. As seen, the storage modulus reduces with decreasing frequency. The slope of G' curves deviate from 2 (terminal behavior) at low frequency by addition modified silica nanoparticles. All the samples presented a higher elasticity and viscosity than those samples without silica. It may be due to their strong segmental interaction, chain entanglement, changing the total interfacial area and relaxation process of the dispersed phase droplets during oscillatory shear flow. The storage modulus and complex viscosity of all the samples enhance with increasing wt. % of modified silica nanoparticles. This may be attributed to improve interfacial interaction between two phases of blends with addition of modified silica nanoparticles compatibilizer that leading to increasing of the elasticity of the blends. A significant difference in the storage modulus and complex viscosity was observed by addition modified silica.

It is well known that the final structure of the blends change by addition a small amount of nanoparticles. The effect of modified nanosilica on blend morphology was determined using SEM analysis. The several studies have been carried out to show that the nanoparticles play a compatibilizing effect in polymer blends.



Figure 3. The storage modulus (G') as function of frequency for the LLDPE/PLA/SiO2 (50/50/SiO2) blends with various wt. % of modified silica nanoparticles.



Figure 4. Complex viscosity versus angular frequency for the LLDPE/PLA/SiO2 (50/50/SiO2) blends with various wt. % of modified silica nanoparticles.

To explain this effect the several mechanism have been proposed as follows. i) decrease of the interfacial energy induced by the nanoparticles, ii) the hinder of coalescence by creation a solid barrier (the nanoparticles) around the dispersed phase, iii) the change of the viscosity of the phases due to an ununiformed distribution of the nanoparticles, iv) the immobility of the dispersed phase (or of the matrix) when the loading of nanoparticles is above a percolation value by the formation of a physical network of nanoparticles, and v) the strong interaction of polymer chains with solid nanoparticles which create steric hindrance²⁴.

Fig. 5 shows the SEM image of the fracture surfaces for the LLDPE/PLA blends with 2 and 8 wt. % of modified silica. As can be seen, the PLA and LLDPE created dropletmatrix morphology for samples without silica due to the high interfacial tension that it leads to the reduction in specific interfacial area. The most of the holes on the sample fracture were created during the fracture process due to week adhesion at interface between the PLA and LLDPE phases. The binary blend without silica (Fig. 5a) shows that the week interfacial adhesion between two phases is due to the hydrophobicity of LLDPE respect to PLA. As seen, the clear boundary interfaces between the dispersed and matrix phases are observed. This indicates strong incompatibility between two phases. Fig. 5b and c present the effect of addition of 2 and 8 wt. % modified nanosilica to LLDPE/PLA sample. The significant change was observed in the morphology of LLDPE/PLA with the presence of 2 wt. % nanosilica. This effect on structure is intensified for LLDPE/PLA with 8 wt. % modified nanosilica. As seen more uniform phase structure was observed in the presence of 8 wt. % nanosilica to the LLDPE/PLA samples. This morphology can be attributed to decrease interfacial tension in the presence of modified nanosilica. It is evident that silica nanoparticles have acted as compatibilizer and improve the interfacial adhesion between two phases. Based on the present results, the morphology of all of the blends nanocomposites have been improved in the presence of the modified silica nanoparticles. In fact the LLDPE/PLA with 8 wt. % of modified silica present the most pronouncing compatibilizing effect. It should be mentioned that the change in the morphology of these blends with the introducing of nanosilica depends on the loading and the distribution of nanosilica in matrix or in the interface of two phases.



Figure 5. The SEM photomicrographs for the LLDPE/PLA (50/50) blend nanocomposites with (a) 0 wt. %, (b) 2wt. % and (c) 8 wt. % modified silica nanoparticles.

CONCLUSION

In this study, the rheological and morphological behavior of the LLDPE/PLA (50/50) blend with different weight percentages of modified silica nanoparticles were investigated. The surface treatment of the silica nanoparticles was performed using reaction improve silanization to hydrophobicity of the nanoparticles. The influence of the modified silica nanoparticles loading (2, 4 and 8 wt. %) on morphological and rheological properties of LLDPE/PLA (50/50) blends was studied. The melt rheology and the SEM results showed that fine morphology were achieved for the LLDPE/PLA with 8 wt. % of modified silica nanoparticles. The linear viscoelastic properties also indicated that incorporation of modified silica nanoparticles into the LLDEP/PLA blend significantly increased the complex viscosity and storage modulus in compared to the virgin LLDPE/PLA. Actually the of silica nanoparticles presence in LLDPE/PLA (50/50) blend have improved dispersion of the minor phase due to increase interfacial adhesion between two phases.

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