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Correlation between Crystallization Behaviour and Interfacial Interactions in Plasticized PLA/POSS Nanocomposites

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Abstract: In this study, the correlation between crystallization behavior and surface chemistry of polyhedral oligomeric silsesquioxanes (POSS) for plasticized poly(lactic acid) (PLA)/POSS nanocomposites was investigated. Four different kinds of POSS particles having different chemical structures were used. Poly(ethylene glycol) (PEG, 8000 g/mol) was utilized as the plasticiser. The nanocomposites were melt-compounded in an Xplore Instruments 15 cc twin screw microcompounder at 180°C barrel temperature and 100 rpm screw speed. Non-isothermal crystallization behaviour of PLA/PEG/POSS nanocomposites were evaluated from common kinetic models such as Avrami and Avrami-Ozawa and Kissinger by using the thermal data obtained from differantial scanning calorimetry (DSC). A polarized optical microscope (POM) equipped with a hot-stage was used to examine the morphology during the crystal growth. In order to investigate the interfacial interactions between POSS particles and plasticized PLA, thermodynamic work of adhesion approach was adopted using the experimentally determined surface energies. A strong correlation was obtained between interfacial chemistry and the nucleation rate in plasticized PLA/POSS nanocomposites. It was found that the polar interactions were the dominating factor which determines the nucleation activity of the POSS particles.

Keywords: PLA, POSS, nanocomposites, non-isothermal crystallization kinetic, interfacial interactions.
PACS: 82.35.Gh

INTRODUCTION

Research and development in biodegradable polymers has received increased attention in recent years because of their wide application in environmental friendly packaging and automotive applications. Poly(lactic acid) (PLA) is one of the well-known materials due to natural biodegradability and availability from renewable resources. Full-scale commercial production of PLA is now a reality; the cost of production has been reduced significantly and PLA is being used in packaging and automotive. However, PLA is a rigid and brittle material in ambient temperature, therefore needs to be plasticized in order to have a tough material. The most common plasticizer used in PLA is poly(ethylene glycol) (PEG). Another disadvantage of PLA is the lack of crystallization ability restricting its versatile applications. Several potential nucleating agents such as organoclays, carbon nanotubes, talc, sodium stearate, calcium lactide, fumed silica nanoparticles were used to increase the crystallization ability of plasticized PLA [1,2]. Alternative to the conventional nanofillers utilized as nucleating agent, poly(hedral oligomeric silsesquioxane) (POSS) nanoparticles have a high potential to increase the crystallization rate of PLA since they have flexible chemical and physical hybrid properties with a reasonably lower price.

Substrate/polymer interfacial interaction plays an important role in the chain conformation and segmental mobility of polymers. For a better understaading of filler/matrix interphase mechanics, it is necessary to determine the interfacial strength and possible interactions between polymer and filler. This is usually carried out by means of contact angle measurements to determine the thermodynamic energy of adhesion formed between filler and polymer [3].

In the current study, it was aimed to investigate the non-isothermal crystallization behavior of POSS reinforced and PEG plasticized PLA by differential scanning calorimeter (DSC) adapting different crystallization methods. Besides, for the first time in literature, correlation between crystallization behavior of PLA/PEG/POSS nanocomposites and thermodynamic adhesion was studied.

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EXPERIMENTAL

Materials

Poly(lactic acid) (PLI005, MFI: 10-30 g/10 min at 190°C/2.16 kg) was purchased from NaturePlast Company, France. Poly(ethylene glycol) (PEG) with the molecular weight of 8000 g/mol (Sigma-Aldrich) was used as a plasticizer in this study. Aminopropylisobutyl-POSS (A-POSS), trisilanolisobutyl-POSS (T-POSS), glycidylisobutyl-POSS (G-POSS) and octaisobutyl-POSS (O-POSS) were purchased from Hybrid Plastics Company, USA (The chemical structures of POSS types used in this study are shown in Table 1). All the POSS types are dissolvable in THF, chloroform and hexane as PLA does, which points out a possible compatibility. They are all in crystalline white powder form. The isobutyl groups on the POSS molecules are responsible from the solubility and compatibility, and the functional groups are responsible for the physical or chemical interaction with the PLA.

Sample Preparation

PLA based nanocomposites, PLA/PEG/A-POSS, PLA/PEG/T-POSS, PLA/PEG/G-POSS and PLA/PEG/O-POSS having different POSS contents (1, 3, 7 and 10 wt %) were prepared via melt blending in a twin-screw microcompounder (15 ml Microcompounder, Xplore Instruments, The Netherlands) at a screw speed of 100 rpm. Before compounding, PLA was dried in an oven at 50 °C for 12 h under vacuum. Prior to processing, predefined amount of POSS, PLA and PEG were dry-mixed. The barrel temperature of microcompounder was set to 180 °C. The mixing time was kept constant at 3 min. Then, the melts were compressed for 3 minute at 180 °C to get films with a thickness of around 0.5 mm. The samples were abbreviated with respect to the type and loading level of POSS, for instance A-POSS1 represents the composite including 1 wt % aminopropylisobutyl-POSS.

Characterization

Contact angles were measured using an Attension Theta Lite model contact angle measurement machine. Bromonaphtalene (BN) was used as the probe liquid for Liftshitz-van der Waals interactions. Ethyleneglycol (EG) and deionized water (DW) were used to identify the acid–base interactions between sample and the probe liquid. The contact angle from each image and the average contact angle for the drop were obtained after each measurement.

Differential scanning calorimeter (DSC) analysis was performed to study the non-isothermal crystallization kinetics of pure PLA, PLA/PEG and PLA/PEG/POSS nanocomposites. The DSC procedure was consisting of three segments. At first segment, the films were heated from 25 to 200 °C with a heating rate of 15 °C/min, then they were held at this temperature for 5 min to eliminate the thermal history, and then they were cooled to 25 °C at cooling rates of 1, 2, 5, 10 and 20 °C/min and held at °C for 5 min. In the last segment, they were reheated to 200 °C at a heating rate of 10 °C/min. Please note that only some selected results were given for non-isothermal crystallization kinetic studies of PLA/PEG/POSS nanocomposites due to the excess of results.

RESULT AND DISCUSSION

Non-Isothermal Crystallization Kinetics

It was obtained from the DSC analysis of neat PLA that it did not exhibit crystallization behavior for higher cooling rates due to the formation of amorphous morphology during cooling process; however, plasticized PLA/POSS nanocomposites tended to crystallize in cooling even for higher cooling rates.

Avrami kinetic model was studied to determine the nucleation type, growth rate and morphology of the crystallite formed for PLA and plasticized PLA nanocomposites. Avrami exponent, n, values found in the case of PLA and PLA/PEG/POSS nanocomposites were in the range of 2-3 and they should possibly be related with two-dimensional growth. Moreover, the highest crystallization rate constant, Z_c, values were obtained from the PLA/PEG/POSS nanocomposites regardless of POSS types at a given cooling rates, which points out much more crystallization rate in the presence of POSS particles.

Another approach for the non-isothermal crystallization kinetic is the combined Avrami and Ozawa model. The values of *F(T)* is the required cooling rate to reach a certain degree of crystallinity for the PLA and its selected nanocomposites is listed in Table 1. As can be seen from the Table 1 that, the highest *F(T)* values were obtained for neat PLA at a given degree of crystallinity. High *F(T)* values indicate higher cooling rates to reach the certain value of crystallinity in the unit time. Therefore, it can be concluded that crystallization rate of PLA/PEG/POSS nanocomposites is faster compared to PLA and PLA/PEG.

TABLE 1. Calculated combined Avrami and Ozawa parameters for PLA, PLA/PEG and selected PLA/PEG/POSS nanocomposites

Sample	X(t) (%)	*F(T)*
PLA	10	3.59
	30	7.56
	50	13.49
	70	33.31
	90	53.07
PLA/PEG	10	5.71
	30	6.97
	50	8.04
	70	9.25
	90	10.81
PLA/PEG/A-POSS1	10	2.30
	30	3.03
	50	3.63
	70	4.34
	90	5.53
PLA/PEG/T-POSS1	10	3.08
	30	4.04
	50	4.88
	70	5.91
	90	7.76
PLA/PEG/G-POSS1	10	3.08
	30	4.45
	50	5.76
	70	7.52
	90	11.53
PLA/PEG/O-POSS1	10	2.88
	30	3.37
	50	3.66
	70	3.92
	90	4.19

Interfacial Interactions by means of Thermodynamic Adhesion

Work of adhesion (W_{AD}) between contacting phases can be calculated by utilizing the contact angles and surface free energy components. It was obtained that G-POSS has a proton rich structure unlike the other POSS types. Thus, W_{AD}^{TOT} value between G-POSS and PLA was obtained higher than that of others due to the presence of acidic epoxy groups, which can interact with electron donor groups of both PLA and PLA/PEG (Table 2). It was found that the interfacial interaction is better between G-POSS/PLA compared to other ones, resulting in adsorption and immobilization of PLA chains on the surface of G-POSS. Consequently, this situation affected PLA crystallization positively in the presence of G-POSS particles.

In order to investigate the presence of a correlation between crystallization behavior and interfacial interactions, Avrami rate constant were plotted versus work of adhesion for PLA/PEG/POSS. The effect of interfacial adhesion on the crystallization rate constant of 3 wt% POSS filled PLA/PEG nanocomposites are shown in Figure 1. One should note that values were obtained for 2 °C/min cooling rate from the Avrami analysis. As can be seen that a

linear correlation was obtained between the crystallization rate and the interfacial adhesion as expected. The highest values for both work of adhesion and crystallization rate constant were obtained from the PLA/PEG/G-POSS nanocomposites.

TABLE 2. Thermodynamic work of adhesion of nanocomposites according to POSS types

Matrix - Particle	Dispersive Component W_{AD}^{LW} (mJ/m^2)	Acid-Base Componenrt W_{AD}^{AB} (mJ/m^2)	Work of Adhesion (W_{AD}^{TOT}) (mJ/m^2)
PLA/PEG - A-POSS	70.4	6.3	76.7
PLA/PEG - T-POSS	72.7	10.0	82.7
PLA/PEG - G-POSS	76.3	17.3	93.6
PLA/PEG - O-POSS	73.8	6.5	80.3

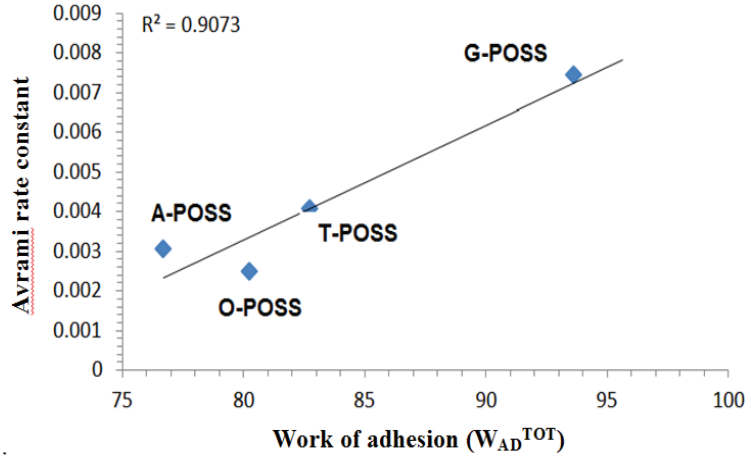


FIGURE 1. Correlation between crystallization rate constant and work of adhesion for PLA/PEG/POSS nanocomposites

CONCLUSIONS

It can be concluded that POSS particles increased the crystallization rate of plasticized PLA by acting as a nucleating agent. The crystal growth of PLA was generally in 2-dimensional in the presence of nucleating agents. Moreover, it was obtained that there is a strong correlation between interfacial strength and nucleation activity.

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