AIP Conference Proceedings

Effects of screw speed on the properties of plasticized PLA/POSS composites

Cite as: AIP Conference Proceedings **1593**, 420 (2014); https://doi.org/10.1063/1.4873812
Published Online: 17 February 2015

M. Kodal, H. Sirin, and G. Ozkoc

View Online Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Correlation between crystallization behaviour and interfacial interactions in plasticized PLA/POSS nanocomposites
AIP Conference Proceedings **1713**, 090002 (2016); https://doi.org/10.1063/1.4942298

Effects of epoxy-POSS nanoparticles on the properties of PLA/TPU blends
AIP Conference Proceedings **1914**, 070005 (2017); https://doi.org/10.1063/1.5016732

Poly(lactic acid) / Poly(ethylene glycol) blends: Mechanical, thermal and morphological properties
AIP Conference Proceedings **1727**, 020002 (2016); https://doi.org/10.1063/1.4945957

Lock-in Amplifiers up to 600 MHz
Watch



AIP Publishing

© 2014 American Institute of Physics.

Effects of Screw Speed on the Properties of Plasticized PLA/POSS Composites

M. Kodal[1], H. Sirin[1] and G. Ozkoc[1]*

[1]*Department of Chemical Engineering, University of Kocaeli, Turkey – mehmet.kodal@kocaeli.edu.tr; humeyra.sirin@gmail.com; guralp.ozkoc@kocaeli.edu.tr*

Abstract
The effect of screw speed on the flow behavior, mechanical, thermal and morphological properties of the melt compounded plasticized poly(lactic acid) (PLA)/polyhedral oligomeric silsesquioxanes (POSS) composites were investigated. Two types of POSS-aminopropylisobutyl-POSS (A-POSS) as the reactive one and the octaisobutyl-POSS (O-POSS) as the non-reactive one, were used at 1-10 wt% filler loadings. Poly(ethylene glycol) (PEG-8000 g/moles) was utilized as a plasticizer. PEG amount was kept constant at 10 wt% with respect to PLA. To investigate the compounding conditions on the properties of the composites, two different screw speeds (100 and 200 rpm) were used. It was found that incorporation of POSS particles to the PLA decreased the melt viscosity of the composites due to the slip-agent behavior of POSS molecules. The mechanical test results showed that composites compounded at 100 rpm have higher yield strength and modulus values. Moreover, a significant improvement in Izod impact strength of plasticized PLA composites compounded at 100 rpm was obtained (regardless of POSS type). SEM analysis showed that POSS particles dispersed homogeneously in polymer matrix at all loadings regardless of screw speed. It was revealed from DSC that POSS particles acted as a nucleating agent for PLA/PEG independently from mixing conditions. Moreover, the percent crystallinity was found to be higher in the presence of POSS.

Keywords: PLA, POSS, plasticization, composite, screw speed

INTRODUCTION

Research and development in biodegradable polymers have received increased attention in recent years because of their possible applications in packaging and automotive applications. Poly(lactic acid) (PLA) is one of the well-known materials due to natural biodegradability and commercially availability from renewable resources. In order to use PLA in packaging applications, it needs to be plasticized [1]. The most common plasticizer used in PLA is poly(ethylene glycol) (PEG) [2, 3]. In order to enhance the stiffness/toughness ratio of plasticized PLA, researchers use the reinforcing particles. Polyhedral oligomeric silsesquioxanes (POSS) nanocages are possible candidates for reinforcement of polymers [4].

In this study, PLA was plasticized with PEG and compounded with two types of POSS, aminopropylisobutyl-POSS (A-POSS) as the reactive one and the octaisobutyl-POSS (O-POSS) as the non-reactive one. The POSS content was varied as 1, 3, 7 and 10 wt %. PEG content was kept constant at 10 wt% in the matrix. The composites were processed at two different screw speeds (100 and 200 rpm). Effects of the screw speed on the mechanical, thermal, morphological properties and flow behavior of composites were investigated.

EXPERIMENTAL

Materials and Sample Preparation

Poly(lactic acid) (PLA, NaturePlast, France) in pellet form with a melt flow index of 10-30 g/10 min. (@ 190 °C, 2.16 kg) was used for the matrix material. Poly (ethylene glycol) (PEG, Sigma-Aldrich) with the molecular weight of 8000 g/mol was used as plasticizer. PEG content was 10 wt% in all composites. PLA/PEG composites were filled with two types of POSS; aminopropylisobutyl-POSS (A-POSS) as the reactive one and the octaisobutyl-POSS (O-POSS) as the non-reactive one. POSSs were purchased from Hybrid Plastic, USA. The POSS content was varied as 1, 3, 7 and 10 wt%. Table 1 shows the chemical structure of POSSs used in this study.

A twin screw microcompounder (15 ml, DSM Xplore model) was used to prepare PLA/PEG, PLA/PEG/A-POSS and PLA/PEG/O-POSS composites. The barrel temperature of microcompounder was set to 180 °C. The compounds were processed at a screw speed of 100 and 200 rpm for 3 min. At the end of this period, the extrudate was injection molded in a DSM Xplore 10 mL injection molding machine at 180 °C and 10 bar. The samples were abbreviated with respect to the type and loading level of POSS, for instance O-POSS3 represents the composite including 3 wt% octaisobutyl-POSS.

Proceedings of PPS-29
AIP Conf. Proc. 1593, 420-423 (2014); doi: 10.1063/1.4873812
2014 AIP Publishing LLC 978-0-7354-1227-9/$30.00

Characterization

Melt viscosity of the composites was determined from vertical force (VF) data recorded in every minute after feeding. The tensile properties were determined using an Instron Universal Testing Machine according to ISO 527. The crosshead speed of 25 mm/min was used. The Izod impact strength was measured with a Zwick/Roell test instrument according to ISO 180. Morphological studies of fracture surfaces of impact samples were carried out using a scanning electron microscope (SEM, JEOL JSM 6060). Differential scanning calorimetry analysis (DSC) were conducted using a Mettler Toledo DSC-1 Star Model instrument between the temperature range of 25°C-190°C with the heating rate of 20 °C/min under nitrogen purging. The percent crystallinity (%X_C) and the nucleation rate of the samples were calculated according to Eq. 1 and Eq. 2, respectively:

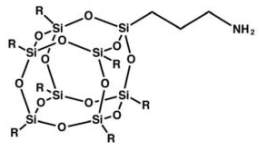
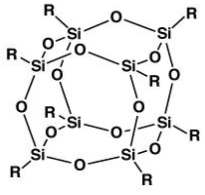
$$\%X_C = \left(\frac{\Delta H_m - \Delta H_C}{\Delta H_m^* \varphi}\right) x100 \quad (1)$$

where ΔH_m is melting enthalpy (J/g), ΔH_c is cold crystallization enthalpy (J/g), ΔH_m^* is heat of fusion for PLA (93 J/g) [5] and φ is the fraction of the PLA in the composite.

$$Nucleation\ rate = T_{cc} - T_{cc,onset} \quad (2)$$

where $T_{cc,onset}$ is the crystallization onset temperature and T_{cc} is the crystallization peak temperature [6].

TABLE 1 Chemical structure of POSSs used in this study

POSS Type	Chemical Structure
Aminopropyl isobutyl-POSS (A-POSS)	
Octaisobutyl-POSS (O-POSS)	 R = *i*-butyl

RESULTS AND DISCUSSION

Vertical force measurement

Vertical force (VF), in other words melt viscosity, during the extrusion was measured to judge the flow properties of the composites. VF of pure PLA decreased with incorporation of PEG. Moreover, VF values of PLA/PEG composites decreased with increasing POSS loadings from 1 to 10 wt% regardless of screw speed as seen in Fig. 1 (a) and Fig. 1 (b). This behavior can be explained by the lubricating effect of POSS particles in PLA matrix [7]. It was also explained in the literature that in the absence of a covalent bonding, the viscosity of the composite decreases with increasing POSS content. The lowering of the viscosity can be an advantage in terms of power consumption during melt processing.

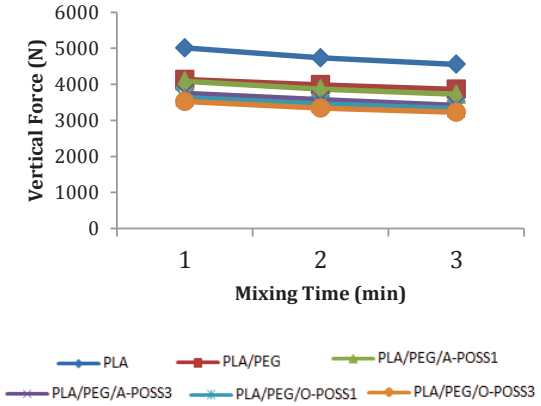


FIGURE 1(a) The variation of vertical force (N) of neat PLA, PLA/PEG and plasticized PLA/POSS composites compounded at 100 rpm

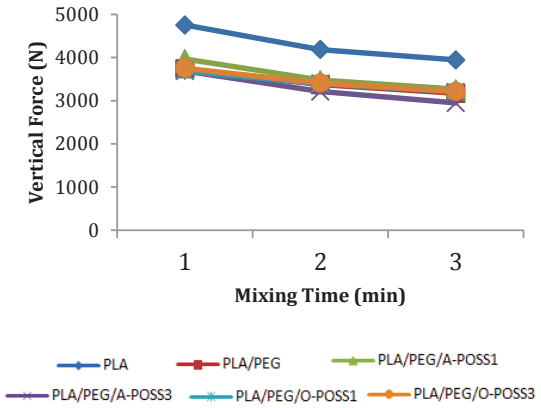


FIGURE 1(b) The variation of vertical force (N) of neat PLA, PLA/PEG and plasticized PLA/POSS composites compounded at 200 rpm

Tensile and impact test results

As seen in Table 2, tensile test results showed a decrease in yield strength and modulus values of neat PLA by the addition of PEG, especially at 200 rpm. PLA/PEG/POSS composites compounded at 100 rpm have higher tensile and impact results compared to composites compounded at 200 rpm. Increasing the screw speed of the micro-compounder adversely affected the tensile and impact properties of all composites. At 100 rpm, there is a slight drop in yield and modulus of PLA/PEG/POSS composites at lower POSS loading levels. However, modulus of PLA/PEG composite was regained 10% and 5%, respectively when 1wt% A-POSS and 1 wt% O-POSS were added. Besides, plasticized PLA/POSS composites have higher strain at break values with respect to PLA and PLA/PEG composites. Moreover, when POSS particles were incorporated to the PLA/PEG matrix, the Izod impact strength of the PLA/PEG composites was significantly improved. This improvement in Izod impact strength was also obtained for PLA/PEG/A-POSS composites compounded at 200 rpm screw speed. In summary, the mechanical analysis showed that enhancement in stiffness/toughness ratio of PLA was achieved by incorporating POSS types into PLA at 100 rpm screw speed.

TABLE 2 Mechanical test results of PLA, PLA/PEG and PLA/PEG/POSS composites

Materials	Screw Speed (rpm)	Yield Strength (MPa)	Modulus (MPa)	Elongation at break (%)	Izod impact strength (kJ/m^2)
PLA	100	73.7	1203	9.1	2.5
PLA/PEG	100	67.5	1105	7.7	3.9
PLA/PEG/ A-POSS1	100	61.2	1191	18.4	3.9
PLA/PEG/ A-POSS7	100	51.7	1121	23.5	4.4
PLA/PEG/ O-POSS1	100	66.5	1159	18.7	3.8
PLA/PEG/ O-POSS7	100	57.3	1057	27.0	4.7
PLA	200	72.5	1203	7.7	3.2
PLA/PEG	200	56.7	961	16.1	3.2
PLA/PEG/ A-POSS1	200	57.8	1008	26.0	3.6
PLA/PEG/ A-POSS3	200	52.0	911	19.9	4.1
PLA/PEG/ O-POSS1	200	53.0	886	15.9	2.9
PLA/PEG/ O-POSS3	200	49.4	925	16.1	3.2

Morphological analysis

SEM analysis showed that PLA fractured in brittle manner during Izod impact testing, which was characterized by larger cracks travel along the sample (Fig. 2). Besides, no phase separation of PEG was observed (Fig. 3). Moreover, A-POSS and O-POSS particles were micron size at 10 wt% loading and homogeneously dispersed in PLA matrix (Fig. 4 and Fig. 5).

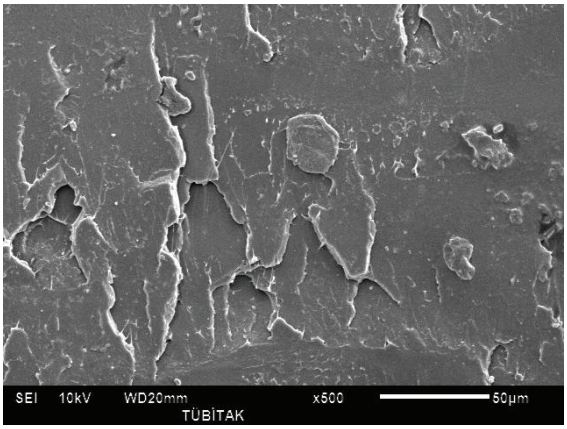


FIGURE 2 SEM micrograph of impact fractured surface of PLA composite compounded at 100 rpm

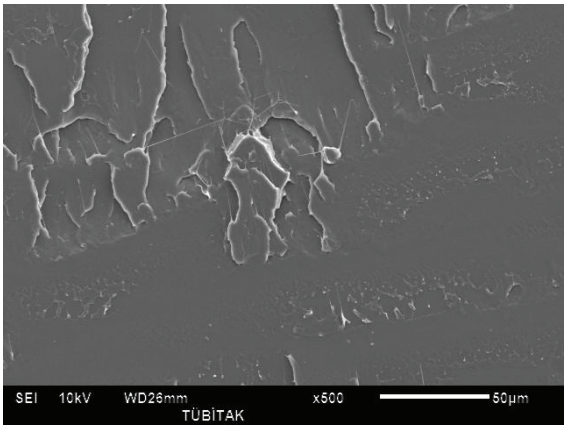


FIGURE 3 SEM micrograph of impact fractured surface of PLA/PEG composite compounded at 100 rpm

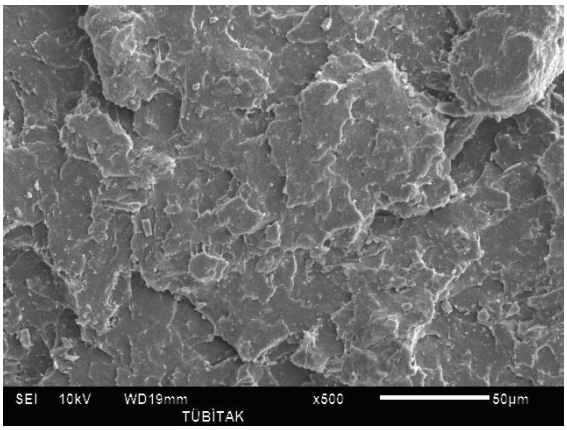


FIGURE 4 SEM micrograph of impact fractured surface of PLA/PEG/A-POSS10 composite compounded at 100 rpm

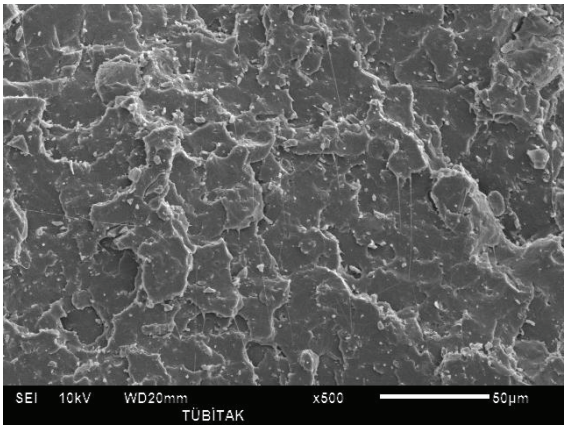


FIGURE 5 SEM micrograph of impact fractured surface of PLA/O-POSS10 composite compounded at 100 rpm

Thermal analysis

All of the prepared composites have similar DSC test results independent of screw speed. So, a summary of DSC test results was shown in Table 3. The addition of 10 wt% PEG into PLA depressed the glass transition temperature (T_g) of PLA due to plasticization. Further reduction in T_g was observed by adding POSS particles to the PLA/PEG matrix. Moreover, POSS particles accelerated the nucleation rate of the pure PLA. The cold crystallization temperature of the composites was depressed by the addition of POSS particles because of the acting as a nucleating agent for PLA crystallization. Percent crysallinity of POSSs filled PLA and PLA/PEG composites were higher than neat one as seen in Table 3.

TABLE 3 Selected DSC Results of PLA, PLA/PEG and PLA/PEG/POSS composites

Materials	Screw Speed	T_g	T_{cc}	$T_{cc,onset}$	T_{cc}-$T_{cc,onset}$	T_m	X_c (%)
PLA	200	59.5	118.9	105.8	13.1	151.9	1.3
PLA/PEG	200	51.4	104.6	97.1	7.5	151.6	6.8
PLA/PEG/ A-POSS1	100	49.3	103.4	93.1	10.3	151.6	10.2
PLA/PEG/ O-POSS1	100	42.9	97.3	88.9	8.3	150.6	7.8
PLA/PEG/ A-POSS3	200	50.3	93.5	89.6	3.9	151.2	7.9
PLA/PEG/ O-POSS3	200	49.2	84.4	80.4	4.0	150.9	12.1

CONCLUSION

The SEM analysis showed that both types of POSS were well dispersed in the PLA regardless of screw speed. Also, addition of both POSS types decreased the melt viscosity of PLA regardless of screw speed. Mechanical tests indicated that composites prepared at 100 rpm have higher yield strength, elastic modulus and Izod impact strength compared to the ones prepared at 200 rpm. Besides, the use of both types of POSS remarkably improved the impact strength of PLA at 100 rpm. DSC analyses showed that glass transition temperature and cold crystallization temperature of PLA decreased by the addition of POSS independently from process conditions. In addition, both POSS types acted as nucleating agent by accelerating the nucleating rate of PLA.

ACKNOWLEDGMENTS

The authors thank to the Scientific and Technological Research Council of Turkey, Tubitak, for supporting this study with contract grant number of 111M514.

REFERENCES

1. N. Ljungberg; B. Wesslen *Biomacromolecules* 2005, *6*, 1789.
2. M. Sheth; R.A. Kumar; V. Dave; R.A. Gross; S.P. McCarthy *J. App. Poly. Sci.* 1997, *66*, 1495.
3. I. Pillin; N. Montrelay; Y. Grohens *Polymer* 2006, *47*, 4676.
4. D. Turan; H. Sirin; G. Ozkoc *J. App. Poly. Sci.* 2011, *121*, 1067.
5. C.D. Migliaresi; D. Cohn; A. De Lollis; L. Fambri *J. App. Poly. Sci.* 1991, *43*, 83.
6. J. Zeng; S. Kumar; S. Iyer; D.A. Schiraldi; R.I. Gonzales; *High Performance Polymers*, 2005, *17*, 403-24.
7. A. Dorigato; A. Pegoretti; C. Migliaresi *J. App. Poly. Sci.* 2009, *114*, 2270.