Journal of Industrial and Engineering Chemistry 31 (2015) 80–85

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Chemical surface modification of lignin particle and its application as filler in the polypropylene composites

Jun-Seok Yeo, Dong-Wook Seong, Seok-Ho Hwang *

Department of Polymer Science & Engineering, Center for Photofunctional Energy Materials, Dankook University, Yongin, Gyeonggi 448-701, Republic of Korea

ARTICLE INFO

Article history:
Received 6 May 2015
Received in revised form 7 June 2015
Accepted 8 June 2015
Available online 20 June 2015

Keywords:
Lignin
Surface modification
Polypropylene
Composite
Filler

ABSTRACT

The pristine lignin was chemically modified by hydrolysis condensation reaction using (3-aminopropyl) triethoxysilane and then was subsequently treated with polypropylene-*graft*-maleic anhydride to give MAPP anchored lignin (MAPP-a-Lignin). The modified lignin particles prepared at each steps were characterized by FT-IR, SEM-EDX and XPS measurements. Polypropylene composites with MAPP-a-Lignin were prepared through melt-blending method. In this work, the effects of content of MAPP-a-Lignin on the properties of the polypropylene composites were investigated. From the results of mechanical properties, melting/crystallization behaviors and the morphologies of the composites, it was found that there was a stronger interfacial interaction between MAPP-a-Lignin and polypropylene in the composites.

Introduction

Lignin is a complicated and non-uniform structure with aromatic alcohols known as monolignols such as *p*-coumaryl, confery and sinapyl alcohol [1]. It mostly occurs in higher plant tissues and is the second most predominant biopolymer present in plants. Since lignin cannot be heated to temperatures greater than 170 °C, at which point degradation takes place, they have limitation to be used in industrial interests [2]. Therefore, they are usually seen as waste products of pulp and paper industry and often used as fuel for the energy balance of the pulping process [3,4]. Hence, the great challenge is to find new utilitarian applications for lignin.

For many years, lignin has been investigated as antioxidant [5–7] and as compatibilizer [8,9] because of a large number of polar functional groups. Utilization as compatibilizer is justified by the presence of both aliphatic and polar groups, which may provide compatibility between non-polar polymers and lignocellulosic fibers. The antioxidant function arises from its chemical structure similar to hindered phenols used as primary antioxidants in polymer industry.

In spite of the utilitarian availability of lignin about lignocellulosic-polymer composites, there is much less information concerning the use of lignin as reinforcement in commodity polymer such as polypropylene (PP) and polyethylene (PE) [10–12]. The effects of adding lignin to polyolefin have been described as changing the surface properties, thermal resistance and biodegradability by acting only as a filler. Lignin has been used in many applications with some success, but the dream of many researchers to use it in large quantities is far from being realized.

This work described a new modification approach for pristine lignin, which had modified its surface by hydrolysis condensation reaction of a triethoxysilane coupling agent, (3-aminopropyl) triethoxysilane, followed by amidation of amine groups with polypropylene-*graft*-maleic anhydride (MAPP) to produce a polypropylene-*graft*-maleic anhydride anchored lignin (MAPP-a-Lignin). This strategy will show the advantage to increase the interface adhesions between the lignin and the synthetic PP matrix that ensure the good physical properties for the composite.

Experimental

Materials

The isotactic polypropylene (iPP) was supplied by LG Chemicals (Korea), [SEETEC H1500, melt flow index (MFI); 12 g/10 min at 230 °C, density; 0.90 g/cm^3]. Organosolv lignin (pH = 6.9–7.1; Ash < 16%) was purchased from BOC Sciences, USA. (3-aminopropyl) triethoxysilane (APS) and polypropylene-*graft*-maleic anhydride

* Corresponding author. Tel.: +82 31 8005 3588; fax: +82 31 8021 7218.
E-mail address: bach@dankook.ac.kr (S.-H. Hwang).

http://dx.doi.org/10.1016/j.jiec.2015.06.010
1226-086X/

(MAPP) pellets (maleic anhydride content: 8–10 wt%, Mw ~ 9100 g/mol) were of reagent grade, obtained commercially from Aldrich. Other dehydrated solvents were purchased from Samchun Chemicals, Korea.

Lignin treatments

A solution of APS was prepared by adding 30 g of APS to 500 ml of a methanol–water mixture (9/1; v/v) and stirred for 30 min. A 10 g of lignin was added to the APS solution and stirred for 4 h at room temperature. The APS coated lignin was filtered and rinsed with distilled water and finally dried *in vacuo* at 50 °C. Then, MAPP was dissolved in xylene at 130 °C. When it was completely dissolved, the APS coated lignin was added in the solution and stirred for 6 h at 130 °C. The lignin mixture was hot-filtered and washed with hot-xylene solvent then kept *in vacuo* at 90 °C for 3 days to evaporate the solvent completely.

Preparation of iPP composites

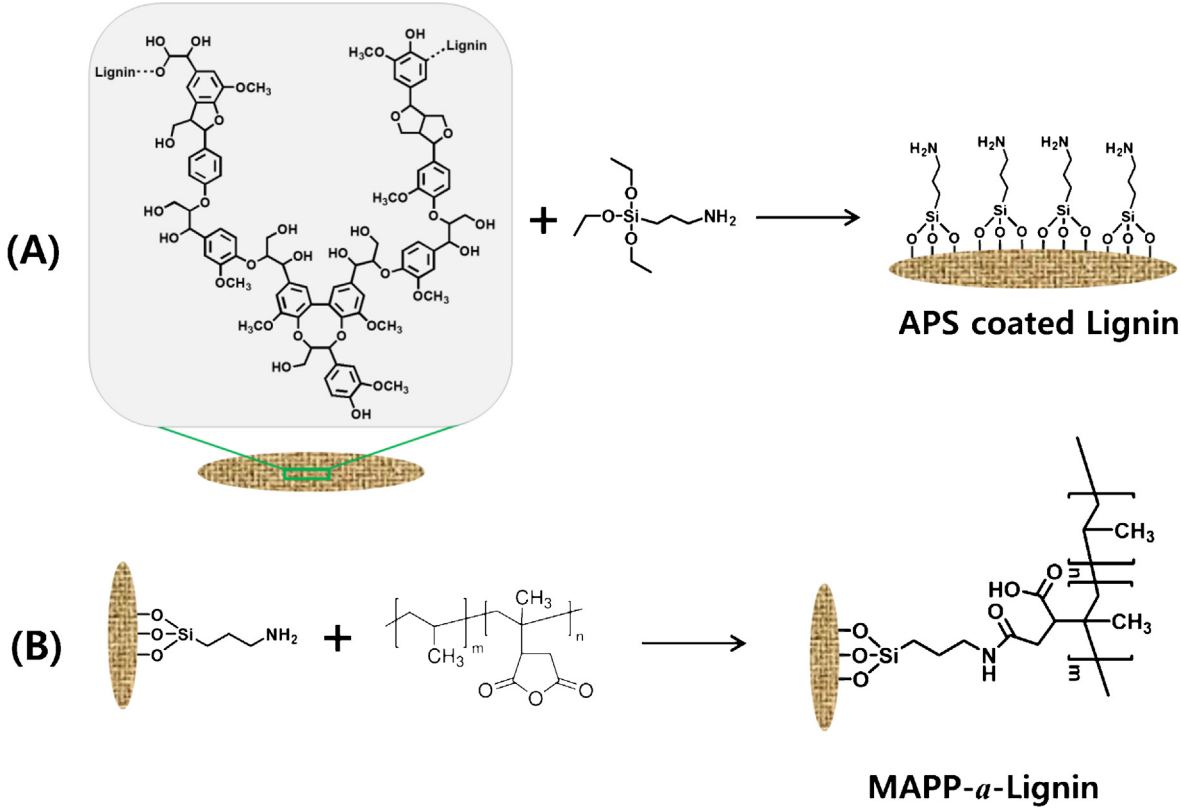
The composites were prepared by melt-mixing MAPP-a-Lignin with neat iPP in the Haake internal mixer (Rheomix 600p). The mass ratios of MAPP-a-Lignin to iPP were 5/95, 10/90, 15/85, 20/80, 25/75 and 30/70. The melt-mixing was carried out at 180 °C and 55 rpm for 10 min. Sheets of about 1 mm thickness were obtained by compression-molding in a Shinto press (Shinto Metal Ind. Ltd., Japan) at 180 °C. Imide films were used to avoid the adhesion of iPP to the stainless surface of the mold. Standard specimens were cut from the pressured sheet for measurement of tensile properties.

Equipment and experimental

The thermal behavior of the phase transitions were studied using a Perkin-Elmer PYRIS Diamond DSC with an Intracooler 2P apparatus. Tensile properties were measured with a Shimadzu AGS-5kNG universal testing machine in accordance with the testing method for tensile properties of plastics (at a crosshead speed of 5 mm/min). The tensile properties were evaluated from the averages of at least four parallel tests. The morphology of the iPP composites were examined using a JSM-7100F Field Emission Scanning Electron Microscope (Jeol, Japan) at 10 kV. The chemical composition of the silane coated lignin was analyzed by using energy dispersive X-ray (EDX, Oxford Instrument) spectrometer attached to the FE-SEM. The XPS spectra were acquired on a K-Alpha (ThermoScientific Co.,) using a monochromatic Al Kα source operating at 72 W.

Results and discussion

Important functional groups, chemical units and inter unit linkages in a lignin are phenolic-OH, aliphatic hydroxyl, carbonyl, alkyl aryl ether, biphenyl, diaryl ether, phenylpropane, guaiacyl, syringyl, *etc*, [13,14]. Among the various functional groups, the hydroxyl group was selected to be used in this work. Because the hydroxyl groups as functional organic moiety on the lignin surface are the reactive sites for silylation, they can play an important role in the surface modification process. These surface chemical modifications for the lignin with APS should help to change the polarity of lignin surface that can hinder their dispersion in hydrophobic polymer matrices. Since a long time ago, it has been well-known from the silicone chemistry that in the presence of moisture, hydrolyzable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group on the surface, forming stable covalent bonds to the surface [15]. Scheme 1(A) represents the desired reaction between lignin surface and APS. In order to better understand the hydrolysis condensation reaction between APS and hydroxyl group on lignin surface, SEM/EDX was conducted to confirm the presence of silicon



Scheme 1. Preparation of polypropylene-*graft*-maleic anhydride anchored lignin (MAPP-a-Lignin) *via* a hydrolysis condensation (A) and amidation reaction (B).