



Original article

Interactions of beech wood–polyethylene mixtures during co-pyrolysis



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ABSTRACT

To investigate the interactions between beech wood (BW) and polyethylene (PE) during co-pyrolysis, they were pyrolyzed both individually and as their mixtures from ambient temperature to 650 °C at a heating rate of 10 °C min⁻¹ using a thermogravimetric analyzer and a tube reactor. In the presence of PE, the production of levoglucosan (LG) and methoxyphenols with unsaturated alkyl side chains from BW was enhanced, resulting in maximum 1.65 and 1.55 times higher yields comparing with their expected yields from BW:PE (w:w)=40:60 mixture, respectively. It was due to the stabilization of the radical species of those by H-abstraction from the PE pyrolysates in the vapor phase. According to this, CO, CO₂, C₂–C₃ compounds, and 5-membered ring compounds, which are LG decomposition products, showed 0.86, 0.85, 0.58, and 0.68 times smaller yields comparing with their expected yields. Methoxyphenols with saturated alkyl side chains, phenols, and catechols, also showed 0.77, 0.66, and 0.87 times smaller yields because they are mainly derived from methoxyphenols with unsaturated alkyl side chains. On the other hand, it was suggested that hydrogen radicals produced during the polyaromatization of BW stabilized PE radical species, resulting in products from PE with higher carbon numbers. Thus, the present work reveals that the interactions between BW and PE mainly involve H-exchange to stabilize radical species. These findings increase our understanding of the operative mechanism in the co-pyrolysis of lignocellulosic biomass and synthetic polymers, which will be useful in future for achieving pyrolysis reaction control and recovering desirable products from difficult-to-separate initial mixtures.

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1. Introduction

Wood-plastic composites (WPCs) display the combined advantages of wood and plastics, such as corrosion resistance, good stiffness properties, and excellent injection-molding processability, while retaining the semblance of wood. The demand for these materials is continually increasing, and they are often used for outdoor decking, automotive parts, siding, fencing, furniture, and so on [1]. Aside from construction wastes, lignocellulosic biomass and plastics mixtures are commonly generated from municipal solid waste streams. Despite their promise as carbon resources for the production of fossil fuel alternatives, the complete separation of such mixtures into wood and plastic by physical means is difficult, resulting in limited treatment methods such as landfilling, incineration, and incineration with energy recovery.

Pyrolysis is a promising method for the conversion of polymeric materials into gases, liquids, and solids, by subjecting them to high temperatures in the absence of oxygen. Pyrolysis can cleave chemical bonds in materials with heat alone, which is of great benefit for treating mixtures of materials which cannot be easily separated. Therefore, pyrolysis has been applied for mixtures of lignocellulosic biomass and plastics. Recently, positive influences of plastic mixing into lignocellulosic biomass have been reported because it improves the carbon and hydrogen content and reduces oxygen content in feed materials, which are often combined with catalytic process. For example, combination with zeolite catalysts enhanced the aromatic and aliphatic hydrocarbon yields in the oil [2–6], combination with the noble metal catalysts and steam improved the yield of H₂ and H₂/CO ratio in syngas [7–10].

The achievement of pyrolysis reaction control can impart significant advantages on subsequent distillation, purification, or catalytic processes because the high yield and selective production of desirable pyrolysates can enable the realization of high-value added products. To achieve this control, a deeper understanding of the pyrolysis reaction mechanism of lignocellulosic biomass and plastics is necessary. Lignocellulosic biomass mainly consists of

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Table 1
Characteristics of BW sample.

Components [wt%]					
Cellulose	Hemicellulose	Lignin	Water	Extractives	Ash
41.6	26.5	23.1	7.0	1.4	0.4
Proximate analysis* [wt%]					
Water	Volatile	Fixed carbon	Ash		
7.0	80.2	12.4	0.4		
Ultimate analysis [wt%]					
Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen**	
49.9	6.2	–	–	43.9	

* On wet basis.

** Calculated by mass difference.

three types of macromolecules that are distinguishable by their monomer units: cellulose, hemicellulose, and lignin. The pyrolysis mechanisms of cellulose [11–14], hemicellulose [15,16], and lignin [17–20] have been updated by a number of authors. Several reports have indicated that these components are decomposed independently during the pyrolysis of woods [21–23]. However, recent research has suggested the existence of interactions between each component [24–29]. The pyrolysis mechanisms of major synthetic polymers such as polyethylene (PE) [30], polypropylene (PP) [31], polystyrene (PS) [32], polyvinylchloride (PVC) [33,34], and poly(ethylene terephthalate) (PET) [35–37] have been previously summarized in detail.

The co-pyrolysis of various combinations of lignocellulosic biomass (cellulose, lignin, beech wood, pine, bamboo, alder wood, red oak, wood sawdust, and almond shells) and synthetic polymer mixtures (high density PE (HDPE), low density PE (LDPE), PP, PS, and PVC) have been investigated in the absence of catalysts [38–55]. For example, Jakab et al. [38] reported that the onset temperature of PP decomposition was lowered in the presence of beech wood (BW) because the char produced from the BW played the role of radical donor in the initiation of PP chain scission. This interaction mechanism was supported by Marin et al. [39], who also studied mixtures of BW and PP. Önal et al. [52] reported that the co-pyrolysis of almond shells and HDPE mixtures at 500 °C synergistically increased oil production. However, Bhattacharya et al. [45] reported that pinewood and synthetic polymers such as PE, PP, and PS were independently decomposed during the co-pyrolysis of their mixtures. In addition, Grieco et al. [47] concluded that there is no important interaction between BW and PE during the co-pyrolysis of their mixtures. Thus, the interactions between lignocellulosic biomass and synthetic polymers have not been completely elucidated, and as such, further investigation is necessary to understand the operative co-pyrolysis mechanisms for these mixtures.

In this work, we selected BW and PE as an example of a common wood and common plastic, respectively. These materials were pyrolyzed, either individually or as various compositional mixtures, from ambient temperature to 650 °C at a heating rate of 10 °C min⁻¹ using a thermogravimetric analyzer (TGA) and a tube reactor.

2. Materials and methods

2.1. Materials

Commercial BW and PE (Sigma-Aldrich, Tokyo, Japan) were ground and sieved to yield particles of less than 250 μm in size. The characteristics of the BW are given in Table 1. The carbon, hydrogen, nitrogen, and sulfur contents were determined using Micro Corder JM10 and Yanako MT-6 elemental analysis systems (J-

Science Lab, Kyoto, Japan). The proximate analysis was carried out using a thermogravimetric analyzer (TG; Seiko Instruments, Tokyo, Japan, TG/DTA6200), following conditions reported previously [7]. Oxygen was assumed to account for the remaining mass. Using procedures detailed elsewhere, the ground BW was dried, extracted with benzene/ethanol (2:1, v/v), and demineralized by washing with 0.05 M HCl/methanol to yield moisture-, extractives-, and ash-free BW [16,56]. The hemicellulose and lignin contents in the prepared “free” BW were determined using previously described methods [57,58]. Finally, the cellulose content was determined by subtracting the moisture, extractives, ash, hemicellulose, and lignin contents.

Other chemicals used in this work were purchased from Kanto Chemical (Tokyo, Japan) and Tokyo Chemical Industry (Tokyo, Japan). Standard gas mixtures containing H₂, CO, CO₂, CH₄, and C₂–C₄ hydrocarbons were purchased from Tanuma Sanso Shoukai KK (Sendai, Japan).

2.2. TG measurements

The weight-loss behavior of mixed samples was investigated thermogravimetrically. A sample (10 mg) was loaded in a Pt pan, in addition to a sapphire plate (10 mg) that was used as reference. After placing the pan into the instrument, the device was purged with helium at a flow rate of 200 mL min⁻¹ for 10 min. Then, the temperature was raised from ambient to 650 °C at a heating rate of 10 °C min⁻¹. The measurements were controlled by Muse 4.1 software (Seiko Instruments).

2.3. Pyrolysis experiments

Pyrolysis experiments were carried out using a horizontal quartz tube reactor heated by an electric furnace. The diagram of the experimental apparatus is published elsewhere [59]. As a minor difference from the previous work, ice and NaOH traps are removed. The prepared BW, free of moisture, extractives, and ash, was used for all experiments to avoid the influence of these components during pyrolysis. Mixed samples prepared with BW:PE (w:w) ratios of 100:0, 60:40, 40:60, and 0:100 were loaded into the ceramic sample holder, which was located in the center of the quartz tube reactor. The air inside of the reactor was replaced by a helium flow of 100 mL min⁻¹, controlled by a digital mass flow controller (FCST1000L, Fujikin, Osaka, Japan). After purging, the temperature was increased from ambient to 650 °C at a heating rate of 10 °C min⁻¹, as controlled by a temperature controller (AGC-9PT, Asahi rika, Chiba, Japan). Pyrolysis products were condensed in a liquid nitrogen-cooled trap or collected in an aluminum bag. As notice, we confirmed that PE completely melts at ~100 °C and BW samples are dispersed in the PE melt. Therefore, we concluded that sample mixing does not influence on the pyrolysis results in the present heating condition.

When the temperature reached 650 °C, heating was stopped and the tube reactor was cooled to ambient temperature under continued helium flow. Then, the cooling trap was defrosted in a water bath, while helium gas was passed through the trap for another 5 min to transfer the previously condensed gases such as CO₂ and CH₄ into the aluminum sample collection bag. The insides of the trap and reactor walls were washed with super dehydrated tetrahydrofuran (20 mL, THF) to remove the collected tar and water (derived from the BW) and the oil and wax (derived from the PE). After washing with THF, the undissolved wax was collected and weighed. The primary char remaining in the sample holder was weighed. The secondary char deposited on the reactor wall was not quantified because it did not dissolve in THF.

The products were defined as (1) gases collected in the aluminum bag; (2) oils that were THF-soluble and derived from PE,

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