

Flame retardancy of biodegradable polymers and biocomposites

Sz. Matkó, A. Toldy, S. Keszei, P. Anna, Gy. Bertalan, Gy. Marosi*

Budapest University of Technology and Economics, Department of Organic Chemical Technology H-1111 Budapest, Műgyetem rkp. 3, Hungary

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Abstract

The efficiency of ammonium polyphosphate in different biocomposites was compared. For the comparison flame retarded lignocellulosic filler reinforced biocomposites were prepared using polypropylene (PP), polyurethane (PUR) and fully biodegradable starch matrices. The compatibility of wood flake with PP was improved by application of an alkoxy silane based reactive surfactant. The silylation improved not only the compatibility but also the thermal stability of the wood flake according to TG measurements. Raman spectroscopic analysis of the silylated product showed that the improved thermal stability is the result of reduced ratio of the amorphous phase of cellulose. The phosphorus additives in flame retarded PUR biocomposites, comprising waste bio fillers and recycled polyol, proved to be very effective because both the matrix and the filler components participate in mechanism of flame retardancy. Plasticised thermoplastic starch could be flame retarded efficiently by as little as 10% ammonium polyphosphate. After their service life the biocomposites can be utilised as chemical fertilizer.

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1. Introduction

One of the biggest challenges of the modern polymer technology is to find replacements for rapidly decreasing non-renewable natural resources and to solve the already burdensome problems of plastic waste management. The growing environmental awareness initiates the development and application of various partially synthetic biocomposites and fully biodegradable polymer systems. One approach is the embedding of natural reinforcing fibres, e.g. flax, ramie, hemp, etc. into synthetic matrices resulting in composites which are not completely biodegradable, but are compatible with the environment [1]. The formation of biocomposites of

totally biodegradable character is a more challenging aim and some results have been already achieved [2–4]. Nevertheless, the most potential short term benefits are expected from the industrial application of combined natural/synthetic polymer systems [5–8].

Natural fibres are considered for use in high technology industries such as transportation and construction as potential replacement for glass fibres, talc and mica in composite materials and for forming structural components of low cost, low density, high toughness and acceptable specific strength [9,10]. There are, however, three factors limiting the use of natural polymers and bio-fibres in engineering fields: low compatibility with hydrophobic polymer matrices, thermal sensitivity at the temperature of compounding processes and flammability, which conflicts with the safety requirements. Although wide scale of surface treatment methods is elaborated to improve the compatibility and strengthen the interfacial interaction,

* Corresponding author.

E-mail address: gmarosi@mail.bme.hu (Gy. Marosi).

the thermal stability and the fire retardancy have been hardly studied [11,12]. Thus the choices of suitable polymer matrices and application fields are limited [13].

The aim of this work was twofold: On one hand to decrease the limitations described above and thus extend the application possibilities of biopolymers/composites. On the other hand to preserve the environmentally-friendly character of the biocomposites even in flame retarded form by using a phosphorus-based system instead of halogen additives. Ammonium polyphosphate (APP), in combination with char forming polyol and nitrogen-containing components are generally called intumescent flame retardants [14–18]. The role of phosphorous compound is to initiate the charring of the polyol. A common feature of the thermoplastic and thermosetting biocomposite systems studied in this work is the charring capability of the reinforcing fibres, matrices or both, which was expected to participate in the flame retardancy mechanism. Information to be obtained by comparing the influence of biodegradable components in various systems may contribute both to understand the mechanism of flame retardancy and to design the biocomposites for engineering use.

2. Experimental

2.1. Materials forming the polymer matrices

Tipplen H535 type polypropylene is a homo-polymer characterised by MFI: 4 g/10 min (230 °C, 2.16 kg) (TVK, Hungary). Polyurethane (PUR) matrix was formed by crosslinking MDI CR-200 type 4,4'-diphenylmethane-diisocyanate (BorsodChem Rt., Hungary) with recycled polyol, (which was produced by decomposition of waste polyurethane elastomer, using mixture of ethylene glycol and diethanolamine). Ruetupox EPD Z8 A/3 type viscosity-lowering component (Kemikál Kft., Hungary) was added to the polyol at 10%. Starch was obtained from corn shell suspension in acetate buffer (0.05 M, pH 4.8) by enzymatic treatment using Thermamyl supra enzyme (Novo Nordisk, Denmark).

2.2. Reinforcing fillers

Natural cotton fibre of 30 mm, wood flake (pinewood as sawdust, assorted of 1.2 mm) and corn shell of 3–12 mm size (Hungrana Kft., Szabadegyháza, Hungary) were used.

Surface treating components were glycerol monooleate (Goldschmidt AG, Germany); tetra ethoxy silane (TES), a colourless liquid of boiling point: 168 °C, density: 0.93 g/cm³, viscosity: 0.65 mPa s (Wacker-Chemie GmbH); and Szilorka K-1 (catalyst of TES),

which consists of tetra ethoxy silane and dibutyl tin dilaurate $\text{Sn}(\text{C}_4\text{H}_9)_2(\text{C}_{12}\text{H}_{25})_2$, melting point: 17 °C, density: 1.05 g/cm³ (Szilor Kft., Hungary).

2.3. Flame retardant components

Exolit 422 ammonium polyphosphate (APP), white powder, average degree of polymerization: 700, acidity of suspension (1% in water): pH 5.5 (Clariant, Germany); $(\text{NH}_4)_2\text{HPO}_4$ (Finomvegyszerkészítő KSZ., Hungary).

3. Methods

3.1. Surface treatments of cellulosic fillers

- A. Silylated natural cellulose (Sil-C) fibre was prepared with 20% TES in presence of catalytic amount of dibutyl tin dilaurate by heating them to 140 °C and keeping at constant temperature until evolution of ethanol was observed. The excess of TES was removed by distillation.
- B. Reactive surfactant (RS) of glycerol monooleate-triethoxy silane type was prepared from 1 mol TES and 1 mol glycerol monooleate in presence of dibutyl tin dilaurate by heating at 120 °C until evolution of ethanol was observed. Molecular mass, determined by the method of boiling point elevation, was 1500 g/mol. RS interphase modifier was introduced into the polymer system in situ during compounding based on earlier results [18].
- C. Treatment of lignocellulosic fillers with $(\text{NH}_4)_2\text{HPO}_4$ was carried out in aqueous solution, then the material was dried under infrared lamp. The mass ratio of the fillers and the flame retardant additive was 1:1.

3.2. Sample preparation

- A. Polypropylene biocomposites were compounded in the mixing chamber 350 of a Brabender Plasti-Corder PL2000 (Brabender, Germany) at a rotor speed of 50 rpm, at 200 °C, with 10 min homogenisation time. Fibres of 30 mass% were previously homogenised physically with surface treating additives, (2% of the fibre weight), then were fed into the PP melt. Sheets (100 × 100 × 3 mm) were formed using a P200E Collin type laboratory compression moulding equipment.
- B. Polyurethane biocomposites were prepared by introducing the wood flake and corn shell fillers into the mixture of recycled polyol and Ruetupox EPD Z8 A/3, then appropriate amount of MDI (molar ratio of polyol to isocyanate was 2:1) was

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