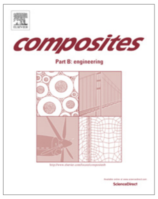
Composites: Part B 68 (2015) 414–423

Contents lists available at ScienceDirect

Composites: Part B

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



Heat treated wood–nylon 6 composites

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ARTICLE INFO

Article history:
Received 27 April 2014
Received in revised form 17 August 2014
Accepted 20 August 2014
Available online 3 September 2014

Keywords:
A. Wood
B. Rheological properties
E. Heat treatment
E. Thermoplastic resin

ABSTRACT

Heat treatment is a relatively benign modification method that is growing as an industrial process to improve hygroscopicity, dimensional stability and biological resistance of lignocellulosic fillers. There also has been increased interest in the use of lignocellulosic fillers in numerous automotive applications. This study investigated the influence of untreated and heat treated wood fillers on the mechanical and rheological properties of wood filled nylon 6 composites for possible under-the-hood applications in the automobile industry where conditions are too severe for commodity plastics to withstand. In this study, exposure of wood to high temperatures (212 °C for 8 h) improved the thermal stability and crystallinity of wood. Heat treated pine and maple filled nylon 6 composites (at 20 wt.% loading) had higher tensile strengths among all formulations and increased tensile strength by 109% and 106% compared to neat nylon 6, respectively. Flexural modulus of elasticity (FMOE) of the neat nylon 6 was 2.34 GPa. The FMOE increased by 101% and 82% with the addition of 30 wt.% heat treated pine and 20 wt.% heat treated maple, where it reached maximum values of 4.71 GPa and 4.27 GPa, respectively. The rheological properties of the composites correlated with the crystallinity of wood fillers after the heat treatment. Wood fillers with high crystallinity after heat treatment contributed to a higher storage modulus, complex viscosity and steady shear viscosity and low loss factor in the composites. This result suggests that heat treatment substantially affects the mechanical and rheological properties of wood filled nylon 6 composites. The mechanical properties and thermogravimetric analysis indicated that the heat treated wood did not show significant thermal degradation under 250 °C, suggesting that the wood-filled nylon composites could be especially relevant in thermally challenging areas such as the manufacture of under-the-hood automobile components.

1. Introduction

Incorporation of lignocellulosic fillers (wood and natural fibers) as reinforcement elements into polymer matrices has received considerable interest from both academic (increasing number of publications and funding sources) and industry (construction and automotive industries) for environmental and economic benefits [1,2]. Lignocellulosic fillers as raw materials for polymer reinforcement presents many advantages compared to mineral fillers, glass fibers and carbon fibers such as low cost, low density, high specific strength and modulus, ease of fiber surface modification, relative non-abrasiveness, renewability and biodegradability, process friendly characteristics, good thermal and acoustic insulating properties, recyclability and world-wide availability [3–8]. A broad range of potential applications of lignocellulosic fillers to high-performance sustainable composites have been developed and these applications are expected to open up opportunities that would allow the replacement of conventional petroleum based-composites with new and improved material properties [9]. However, despite active research activities and their attractive properties, there are several obstacles to overcome for the use of lignocellulosic fillers, including (1) the issue of compatibility between hydrophilic lignocellulosic fillers and hydrophobic polymers, (2) hygroscopicity and dimensional changes because of its hydrophilic nature, (3) uniform dispersion and extreme agglomeration and (4) low thermal stability, limiting its applications in engineering thermoplastics which have high melting points [9–11].

Engineering thermoplastics are playing a growing role in "under-the-hood" components for automobiles that are competing

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http://dx.doi.org/10.1016/j.compositesb.2014.08.040
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with incumbent materials (metal and thermoset plastics) because their excellent mechanical and thermal properties [12]. Nylon 6 (PA 6) is in a major class of engineering thermoplastics and the use of nylon 6 in natural fiber composites presents some advantages: (1) higher mechanical properties of nylon as compared with polyolefins, because of its hydrophilic nature, great compatibility between nylon and lignocellulosic fillers and (2) easier to recycle than thermosets, which remain competitive with nylon in under-the-hood applications in North American markets [6,12,13]. In spite of the industrial interest in nylon 6 especially in the automotive industry and recent efforts which have demonstrated the feasibility of producing nylon/lignocellulosic composites, there is lack of information related to lignocellulosic filler reinforced nylon composites because of the difficulties in producing the composites without considerable thermal degradation of lignocellulosic fillers and high cost of nylon compared to commodity plastics [5,6,13–20].

Hygroscopicity and dimensional changes are identified as significant drawbacks of lignocellulosic composites exposed to environmental conditions [8]. To minimize these drawbacks and to increase the number of lignocellulosic composites products with new and improved material properties for different applications, improvements are needed (Segerholm 2007). To eliminate these drawbacks, many studies including different modification methods have been performed during the past several decades. It appears that two main methods were investigated. The chemical modification or surface functionalization of fillers has been the least convenient because these methods are chemically-based, time consuming and fastidious to process [7,8]. Heat treatment is a modification method that is growing as an industrial process to improve hygroscopicity, dimensional stability and biological resistance of lignocellulosic fillers without contaminating the environment [2,4,7,8,21]. During heat treatment, there are considerable changes in the chemical composition of the fillers including: (1) decomposition of hemicelluloses (the most hydrophilic component of the cell wall) and lignin, (2) release of acetic acid, which is one of the main by-products and accelerates further carbohydrate depolymerization and (3) lignin modification which allows increased cross-linking in the lignin-carbohydrate complex [7,8]. Heat treatment also has its own drawbacks including reduction of mechanical properties, unwanted color and odor [3,4]. Adding heat treated lignocellulosic fillers should also lead to an improvement in the thermal stability of the polymer composites because its sensitive components are decomposed or at least have gone through structural changes during the treatment [3]. By taking this feature into account, heat treatment can improve engineering thermoplastic composite properties more than untreated lignocellulosic fillers because of their higher thermal stability.

In spite of the academic and industrial interest in heat treated wood, only a few studies of heat treated lignocellulosic filled-polymer composites have been published in the literature. Most polymers used in heat-treated wood filled polymer composites are polyolefin (polyethylene (PE) and polypropylene (PP)) based materials (Table 1). To the best of authors' knowledge, heat treated lignocellulosic filled engineering thermoplastic composites have not yet been reported in the literature. Most results from the literature show that the water uptake, dimensional expansion and biological durability (no or slight attack by fungi) of polymer composites based on heat treated lignocellulosic fillers were significantly reduced while no improvement in mechanical properties especially in strength was observed [7,8,24,28]. Most studies were also concerned with mechanical, morphological and water absorption properties (Table 1) and there is a lack information related to rheological properties of heat treated lignocellulosic filled polymer composites in the literature. In this paper, the rheological properties of nylon 6 composites with different heat treated wood filler loadings is systematically studied to investigate the effect of heat modification on the rheological properties of the nylon 6 matrix. The objective of this paper is to establish and optimize a production process for engineering thermoplastic composites based on heat treated wood fillers and nylon 6, suitable for automotive applications, especially under-hood applications. The present paper also addresses the effect of the heat treated wood fillers on the mechanical and rheological properties of nylon 6 at different filler loading levels.

2. Experimental

2.1. Materials

The nylon 6 used as the matrix was supplied by Entec Co., USA. Nylon 6 has a density of 1.13 g/cm^3 and mold shrinkage 0.4 mm/mm. The lubricant (Struktol TPW 113) processing aid, being a blend of a complex, modified fatty acid esters and having a specific gravity of 1.005 g/cm^3 and drooping point of 67–77 °C respectively, was supplied by Struktol Company of America. Red maple (*Acer rubrum* L.) and eastern white pine (*Pinus strobus* L.) used as fillers in the study were kindly supplied by the Advanced Structures and Composites Center.

2.2. Heat treatment

Heat treatment was done in the presence of water vapor and air at atmospheric pressure in a conventional oven that had a sensitivity of ±1 °C. The heat treatment was conducted at 212 °C for 8 h in an attempt to increase the durability of the wood materials. After heat treatment, the solid wood board samples were removed from the oven and ground in a grinder. Wood flour of pine and maple greater than 60 mesh were used as raw materials to prepare the wood flour/nylon 6 composites.

2.3. Processing of composite materials

The untreated wood flour, heat treated wood flour and nylon 6 were dried to a moisture content of less than one percent using an oven at 105 °C for 16-h. The matrix polymer, nylon 6, was mixed with the untreated wood flour, or heat treated wood flour. The compounding was conducted with a Brabender Prep-mixer® equipped with a bowl mixer and the process temperature was measured in real time. The temperature was set at 230 °C and rotor speed at 60 rpm. The untreated wood flour, heat treated wood flour were added to the mixer when the polymer appeared well melted. Mixing was done for 15 min until the torque stabilized. The nylon 6–wood flour compounds were granulated using a lab-scale grinder. The ground particles were dried in an oven at 105 °C for 16 h before being injection molded into ASTM test specimens. All materials were injection molded using a barrel temperature of 230 °C mold temperature of 230 °C injection pressure of 2500 psi. The compositions of the composites are shown in Table 2.

2.4. Characterization

2.4.1. Thermogravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) measurements were carried out using a Mettler Toledo analyzer on samples of about 10 mg. Each sample was scanned over a temperature range from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen with a flow rate 20 ml/min to avoid sample oxidation. The samples used for the TGA measurements were 5 randomly picked from the ground test specimens. To eliminate the buoyancy effect,