



A universal route towards thermoplastic lignin composites with improved mechanical properties



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ARTICLE INFO

Article history:

Received 11 October 2013

Received in revised form

20 December 2013

Accepted 29 December 2013

Available online 8 January 2014

Keywords:

Lignin

Nanocomposite

ATRP

ABSTRACT

Nanocomposites based on synthetic polymers grafted from kraft lignin with average particle size of 5 nm were synthesized using atom transfer radical polymerization (ATRP). Lignin macroinitiators were prepared, and polystyrene and poly(methyl methacrylate) were polymerized with target degree of polymerization of 450 resulting in materials having lignin mass fractions of 4.5%, 8.3%, and 22.1% for the poly(methyl methacrylate) samples and 3.2%, 7.1%, and 19.6% for the polystyrene samples. Tensile testing showed a decreased modulus but enhanced toughness of all nanocomposites compared to homopolymers, and the poly(methyl methacrylate)-grafted samples had nearly twice the ultimate elongation as the polystyrene grafts at high graft density. Both types of grafted nanocomposites had toughness values that were greater than 10-times that of the corresponding kraft-lignin/polymer blend system, indicating the potential of ATRP as the basis for the 'one component' composite approach towards more sustainable polymeric materials. Dynamical mechanical analysis was used to measure softening temperatures, and both the polystyrene-grafted and poly(methyl methacrylate)-grafted nanocomposites had a peak in the loss modulus that was higher than the corresponding homopolymer, consistent with strong polymer–lignin interactions. Lignin grafted with thermoplastic polymers could be an important material based on an inexpensive, renewable feedstock that offers unique mechanical properties compared with many other nanocomposites based on inorganic nanoparticles. Our results indicate that ATRP is well suited for preparing lignin-based thermoplastics and could be the basis for hybrid materials that make effective use of this important renewable resource.

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1. Introduction

The integration of natural-sourced polymers with synthetic commodity and engineering plastics is widely recognized to be an important cornerstone in the broader context of developing more sustainable and low-energy polymeric materials [1–8]. Kraft lignin – a term used to describe a range of polydisperse and branched phenolic polymers that are derived from native lignin via the kraft pulping process – has received particular attention due to the relevance of lignin as medium for solar energy storage in plants and its abundance as an important structural component of wood. The high thermal, oxidative, and hydrolytic [9] stability as well as favorable mechanical properties (the Young's modulus has been

estimated to 2 GPa [10]) have motivated interest in using kraft lignin as a filler, for example, for the reinforcement of elastomeric materials [11–18]. However, while the application of lignin in elastomeric as well as thermoset material systems has been widely reported [19], its application as filler in thermoplastic polymeric systems has been a challenge. Among the relevant nonpolar engineering polymer systems, best results were achieved by blending kraft lignin with poly(methyl methacrylate) (PMMA). For example, blends containing 5–20% hydroxypropyl lignin in PMMA were found to have single glass transition temperatures that were around 5 °C below that of pure PMMA and a Young's modulus of 1800–1900 MPa, depending on lignin molecular weight and mass fraction in the blend [20]. This value of Young's modulus represented a 200 MPa increase over the pure polymer, however, all blends were found to be brittle with a strain-to-fracture less than 2%. The limited effect of kraft lignin was rationalized as a consequence of the poor interfacial binding between filler particles and the matrix that favors particle aggregation and phase separation in

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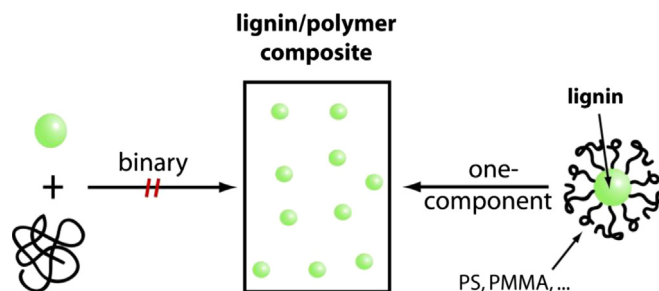
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lignin/polymer blends [21–26]. The development of novel synthetic strategies to facilitate miscible polymer/lignin blends is therefore an important challenge to realize the potential benefits of lignin filler materials for the development of thermoplastic polymer blends.

The challenge of facilitating miscible kraft lignin dispersions bears similarity to the broader challenge of understanding the governing parameters that control miscibility in particle/polymer blends [23]. The latter systems have received particular attention in the context of inorganic particle/polymer dispersions. A widely used strategy to compatibilize particle fillers within polymeric hosts is by grafting of polymer chains that are chemically identical to the matrix polymer to the particle matrix [27,28]. In these athermal polymer/particle blends mixing is determined by the subtle interplay of entropic contributions that sensitively depend on the architecture of the polymer-grafted filler (i.e. the density and degree of polymerization of grafted chains as well as the particle size). In general, miscibility is expected only if the degree of polymerization of grafted chains is at least of the same order as the matrix [29]. As recently demonstrated by Ojha et al., [30] the requirement of high molecular grafted chains severely limits the attainable filler concentration and thus the blending of polymer-grafted (lignin) fillers with the corresponding matrix polymers cannot be seen as a viable strategy towards lignin/polymer composites with high lignin content and improved property characteristics.

An alternative strategy to attain high filler content polymer nanocomposites is based on the concept of ‘one-component’ hybrid materials – nanocomposite materials that are synthesized by the assembly of polymer-grafted particles [31]. Primary advantages of the ‘one-component’ approach are the fine control of the materials microstructure (note that miscibility gaps are absent in one-component systems) along with mechanical properties that resemble those of higher molecular weight polymers. Due to their technological relevance as commodity and engineering plastics as well as the accessibility to viable controlled radical polymerization techniques, polystyrene (PS) and PMMA have been studied extensively as model systems in one-component nanocomposites. For example, Choi et al. recently demonstrated that the assembly of PMMA- or polystyrene- (PS) grafted silica particles with suitable architecture enables the fabrication of nanocomposite materials with highly regular microstructure [32]. Interestingly, one-component nanocomposites were found to exhibit significantly increased fracture toughness (as compared to the corresponding binary particle/polymer blend systems) – this characteristic was explained as a consequence of the more effective entanglement structure in branched polymeric systems [33]. We note that a particular advantage of the ‘one-component’ approach towards nanocomposite materials is that it is applicable to any type of ‘matrix’ polymer as long as synthetic methodologies exist to facilitate the controlled grafting of the polymer to the particle system. The general concept of one-component nanocomposite materials is illustrated in Scheme 1.

The objective of this article is to illustrate the application of ATRP in preparing thermoplastic ‘one-component composites’ that combine a high filling fraction of lignin with improved fracture resistance as compared to the binary polymer/lignin blend systems. The structure of this paper is as follows: In the first part we discuss the conditions that allow for application of atom-transfer radical polymerization to synthesize a set of PMMA- and PS-grafted lignin particle systems with systematic variation of the number and degree of polymerization of surface grafted chains. In the second part we discuss the effect of polymer graft modification on the mechanical properties of lignin-based one-component composites and we demonstrate that even in case of lowest density of polymer



Scheme 1. Comparison of ‘binary’ and ‘one-component’ nanocomposite fabrication schemes.

grafts per lignin ‘particle’ a significant improvement of fracture resistance as compared to ‘classical’ binary composites was observed. Thus, polymer-grafted lignin particles with appropriate architecture could present a novel platform for the fabrication of low-energy thermoplastic commodity polymers with high lignin content and enhanced mechanical properties.

2. Experimental section

2.1. Materials

Lignin was purchased from Tokyo Chemical Industry, Co. Methyl methacrylate (MMA), styrene, ethyl 2-bromoisobutyrate (EBiB), CuCl, CuBr, N,N,N',N'-pentamethyldiethylenetriamine (PMDETA), 2,2'-bipyridine (bpy), and pentafluorobenzaldehyde were purchased from Sigma–Aldrich. Styrene and MMA monomers were run through a basic alumina column before use to remove inhibitor. All other chemicals were used as received.

2.2. ATRP of styrene

First, styrene, dimethylformamide (DMF), PMDETA, and EBiB were dried over molecular sieves and degassed under nitrogen for 30 min. Then CuBr (14.8 mg, 0.103 mmol) was added to a 50 mL Schlenk flask, which was subsequently degassed by three vacuum–nitrogen cycles. Next, 4.5 mL DMF, 21.5 μ L (0.103 mmol) PMDETA, 5.31 mL (46.3 mmol) styrene, and 15.1 μ L (0.103 mmol) EBiB were added to the flask and the reaction was carried out at 100 °C for 7 days. The percent conversion was determined to be 52% using ^1H NMR by comparing the disappearance of acrylate peaks to DMF internal standard. Copper was removed by dilution with THF and filtration through neutral alumina. The polymer was precipitated into 100 mL of hexane and dried *in vacuo* at room temperature. The resulting polymer (1.2401 g, 51.4% yield) was a white brittle solid.

2.3. ATRP of methyl methacrylate

ATRP of MMA was conducted in the same manner as described above. First, MMA, DMF, PMDETA, and EBiB were bubbled under nitrogen for 30 min and 17 mg (0.119 mmol) of CuBr was added to a Schlenk flask with three vacuum–nitrogen cycles. MMA (5.03 mL, 47.2 mmol), 1.2 mL DMF, PMDETA (21.9 μ L, 0.105 mmol), and EBiB (15.4 μ L, 0.105 mmol) were added and the reaction was carried out at 70 °C for 24 h. Percent conversion according ^1H NMR was 62%. Again, copper was removed by dilution with THF and filtration through neutral alumina. A total of 1.9543 g (66.7% yield) was obtained after precipitation into hexane and drying *in vacuo*.

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