Hybrid fillers of lignin and carbon black for lowering of viscoelastic loss in rubber compounds

Kushal Bahl [a], Toshikazu Miyoshi [b], Sadhan C. Jana [a, *]

[a] Department of Polymer Engineering, University of Akron, Akron, OH 44325-0301, USA
[b] Department of Polymer Science, University of Akron, Akron, OH 44325-3909, USA

A B S T R A C T

This study investigates novel hybrid fillers for lowering of viscoelastic dissipation in rubber compounds by exploiting non-covalent interactions between lignin and carbon black (CB). Lignin is naturally occurring three-dimensional amorphous polymer consisting of phenyl propane units with hydroxyl, methoxy, and carbonyl substitutions and is capable of producing non-covalent interactions via $\pi-\pi$ stacking with CB particles. The hybrid fillers are obtained by precipitating lignin from solutions onto carbon black particles. The fractal nature similar to CB particles and the presence of lignin coating layers on CB particles are confirmed by electron microscopy images. The coating layers are promoted by strong $\pi-\pi$ interactions as revealed from Raman spectroscopy and ^{1}H spin-lattice relaxation data and supported by a drop in zeta potential values. The hybrid fillers show much less networking than CB and reduce the viscoelastic dissipation in model rubber compounds by as much as 10% in comparison to the compounds of only CB.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Lignin is amorphous polymer derived from wood consisting of a phenylpropanoid backbone along with phenolic and benzylic hydroxyl, methoxyl, and carbonyl substitutions [1]. They are one of the primary constituents of woody stems in plants apart from cellulose and hemicellulose and hence are the second most abundant renewable material available on earth behind cellulose [2,3]. It imparts rigidity and impact strength to the cell walls in plants by binding the cells together [3,4]. The abundance of functional groups on its surfaces is one of the reasons why it is widely studied as reinforcing filler of plastics and rubber. Note in this context that the functional groups provide scope for chemical modification and adjustment of polarity to produce compatibility with appropriate matrix polymers [5,6]. In conjunction, the natural abundance, cost competitiveness, and biodegradability [7] make lignin attractive for development of plastic and rubber composites. Recent studies on the use of lignin in composites of thermosets, thermoplastics,

elastomers, and foam materials have been well documented by Thakur et al. [8].

Nevertheless, large particle size and naturally occurring polarity are two responsible factors against more widespread usage of lignin as a filler [6]. The spray drying process during delignification of cellulose limits the particle size of lignin [9]. Commercial lignin shows particle sizes ranging from 10 μm to greater than 100 μm. Such particles are large and they increase the viscosity of compounds via hydrodynamic effects [10] and exhibit detrimental impacts on mechanical properties. The above factors limit the usage of lignin as a "drop in" replacement for conventional fillers in development of compounds of polymers and elastomers.

Some researchers demonstrated several means of reduction of particle size of lignin, for example, by digesting lignin in the presence of protic acid [11], promoting self-assembly of lignin with cationic polyelectrolytes in aqueous solution [12], or by co-precipitation [13]. However, digestion in acid leads to degradation and breakdown of lignin [14] which can also lead to a loss of its reinforcing abilities. On the other hand, the processes of co-precipitation and self-assembly with polyelectrolytes involve the use of aqueous media, which are deterrent to development of rubber compounds. In this work, a new and novel means is examined for alleviating two concerns associated with the use of

lignin and carbon black in rubber compounds. The first concern relates to large particle size of lignin and the second concern relates to networking of carbon black particles in rubber compounds and large viscoelastic dissipation. Both these concerns are alleviated in this study by developing hybrid fillers from lignin and carbon black.

Hybrid fillers are vastly useful in rubber compounds for suppression of filler networking whereby the probability of particle–particle contacts and formation of particle networks is greatly reduced [15]. The filler network formation and associated network breakdown in rubber compounds with strain lead to energy dissipation and conversion of such dissipated energy into heat. A consequence of such energy dissipation is an increase of the rolling resistance of rubber compounds [15]. Thus, efforts to increase the energy efficiency and to reduce the rolling resistance should consider suppression of filler particle networking in carbon black filled rubber compounds.

Ismail et al. [16] reported improved mechanical and fatigue life performance in compounds of dry mixed, 29:1 by weight, silica and carbon nanotube hybrid filler compared to silica. Sapkota et al. [17] observed reduction of Payne effect and storage modulus at lower strains by partially substituting carbon black with clay in compounds of natural rubber. These mixed fillers showed reduction of filler networking, although insufficient dispersion of clay particles led to reduction of tensile properties. The synergy between carbon nanotubes and carbon black in their hybrid fillers led not only to increases in storage modulus values but also in the values of loss tangent in compounds with polyisoprene [18]. It is apparent that the synergy among filler particles does not always produce the desired effects. The most significant work on hybrid fillers was reported by Wang et al. [19]. These authors developed carbon black-silica dual phase filler to obtain better mechanical properties and an optimum balance of tire properties such as rolling resistance, wet traction, and wear resistance. Despite reporting successful implementation of hybrid fillers, fundamental understanding of why particular sets of hybrid fillers work or how research should be guided in the design of new hybrid filler systems is still missing.

The interactions of lignin, specifically sodium lignosulfonates (SLS), with carbon nanotubes were studied by Liu et al. [20]. These authors obtained stable aqueous dispersions of multi-walled carbon nanotubes (MWNTs) by grinding the MWNTs with SLS and attributed such stable dispersion to adsorption of SLS on the nanotube surfaces due to π–π stacking. A similar study dealing with surface functionalization of MWNTs using kraft lignin and its use in energy storage applications was also reported by Milczarek and Nowicki [21]. However, no studies exist on interactions between lignin and carbon black particles, their unique morphologies, or their applications in development of rubber compounds. As is apparent from discussion of prior work, research efforts exist on the use of combinations of carbon black, carbon nanotubes, and silica as hybrid fillers. However, very little work exists on development of bio-derived materials from plant sources and agricultural wastes as a component in hybrid filler systems for rubber compounds. Efforts to combine lignocellulosic materials in hybrid fillers for rubber compounds met with limited success. Attharangsan et al. [22] reported drops in the values of tensile strength, 100% modulus, and fatigue life in compounds of rubber with hybrid fillers of rice husk powder and carbon black apparently due to poor filler particle adhesion with rubber and large particle size of the rice husk powder (~12 μm).

In this work, the interactions between lignin and carbon black are first characterized using electron microscopy and spectroscopic techniques and then exploited in the development of hybrid filler systems for model rubber compounds.

2. Experimental

2.1. Materials

Two types of lignin particles were used in this work – kraft lignin (KL) powder from Weyerhaeuser (Federal Way, Washington) with molecular weight (M_w) ~5090 g/mol, polydispersity index ~5.4, and glass transition temperature (T_g) ~128 °C and calcium lignosulfonate D618 (LS) particles obtained from Borregaard Lignotech (Rothschild, Wisconsin). The generic structure of these lignin molecules is the same. However, the sulfonate groups in LS particles promote its solubility in water. Carbon black grade N330 manufactured by Sid Richardson (Fort Worth, TX) and styrene butadiene rubber (SBR), grade SLF18B10 obtained from Goodyear Tire and Rubber Co. were used in preparation of rubber compounds. The SBR contained 18.5 wt% styrene. The rubber curing package included zinc oxide powder, stearic acid in bead form, sulfur curing agent (Rubber Maker), and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) accelerator, all obtained from Akrochem Corporation (Akron, OH).

2.2. Preparation of lignin-carbon black hybrid particles

Two types of hybrid fillers were prepared. The first hybrid fillers of KL and CB, designated as KL-CB, were prepared by dissolving KL in a solvent and dispersing CB in the solution using ultrasound. For this purpose, acetone was used as the solvent for preparation of hybrid particles for transmission electron microscopy while 0.5 M NH_4OH was used as the solvent for hybrid fillers used in surface area measurement. The fillers were recovered by evaporating the solvent and used in characterization by transmission electron microscopy (TEM) and Brauner–Emmett–Teller (BET) surface area analyzer. KL-CB particles were not used in preparation of rubber compounds. The second type of hybrid fillers, designated as LS-CB particles, was prepared from LS and CB. Carbon black particles were dispersed in solutions of LS in water by ultrasound for 30 min. The solid hybrid particles were recovered by slowly evaporating water and then drying the residue in vacuum oven at 80 °C for 24 h. The particle agglomerates were milled to size below 100 μm and were used in preparation of rubber compounds. The LS-CB particles in rubber compounds contained LS and CB in the weight ratio 10:90 and 20:80, while LS-CB particles used in characterization by Raman spectroscopy contained LS and CB in weight ratio 3:1 and 1:1. A higher lignin concentration in specimens for Raman spectroscopy accentuated the interactions and resulted in higher signal fidelity.

2.3. Rubber compound preparation

Rubber compounds of hybrid fillers were prepared in two steps. In first step, rubber was mixed with zinc oxide, stearic acid, and hybrid filler particles in a Brabender Plasticorder internal mixer of 80 cm³ volume at a rotor speed of 65 rpm and a fill factor of 0.7 at 80 °C. The rubber was masticated for 60 s and mixed with the rest of the ingredients for 5 min. The compounds obtained in step 1 were mixed with sulfur and CBS accelerator in a two-roll mill for 5–7 min at a speed of 15 rpm and a roll temperature of 40 °C. The rubber compounds contained the following ingredients based on 100 parts of SBR 1 phr stearic acid, 3 phr zinc oxide, 1.75 phr sulfur, 1 phr CBS, and 30 phr hybrid filler, where phr designates parts per hundred rubber. A control material was also prepared by compounding SBR and 30 phr of carbon black in the same manner. The flocculation of filler particles was studied using compounds of hybrid fillers and SBR with no curatives.