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Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin

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ABSTRACT

Lignin have been esterified using phthalic anhydride and then blended with (up to 40 wt.%) low density polyethylene (LDPE). Maleic anhydride grafted LDPE has been added as compatibilizer. The mechanical and thermal properties of the blends were measured according to ASTM standards and compared with those of neat LDPE. The results reveal that addition of compatibilizer improved the mechanical properties significantly approaching values close to those of neat LDPE. The scanning electron micrographs of the blend specimens also support the above observations. Thermogravimetric analysis showed greater thermal stability for the compatibilized blends. The char content has been found to increase with increasing filler (lignin phthalate) content. DSC analysis revealed that the crystallinity values of the blends slightly increase by the addition of filler (lignin phthalate).

1. Introduction

Biobased composites have gained prominence over the past two decades owing to both environmental concerns as well as waste disposal problems. Among the various thermoplastics, low density polyethylene (LDPE) and polypropylene have the largest tonnage in the world and their per capita consumption is continuously on the rise.

There are many options to adopt environment friendly solutions and among them one is to use microbial polyesters such as polyhydroxybutyrate but their cost is a limiting factor.

The other alternative is to load the polyolefins with as much of biopolymer as possible along with pro-oxidant additives. However, a blend of a polyolefin like LDPE with a biopolymer would not be compatible due to the inherent differences in their physical and chemical properties. Among the various biopolymers, starch, cellulose, chitosan, low quality wood such as rubber wood are being extensively used. Among these lignocellulosic materials are available in abundance. Further, waste materials such as lignin are underutilized natural resources. Updated reviews on biodegradable composites based on lignocellulosic fibers have been reported by Satyanarayana et al. [1]. Biocomposites by hydrolysis of lignocellulosic substrates was studied by Vila et al. [2]. Development of modified lignin based eco-friendly products was carried out by Sena-Martins et al. [3]. Similar studies on utilization of lignins to develop value added biocomposites was analyzed by Steward [4]. A major limitation of these lignocellulosic materials is their hydrophilicity. Hence a modification of these materials will enhance barrier and mechanical properties. Superficial modification of blue agave fiber was carried out via esterification in order to enhance interfacial bonding with high density polyethylene [5].

The performance of lignin polymers and composites has been analyzed by Wool and Sun [6]. Benzylated sisal fiber/synthetic polymer composites were found to have improved mechanical properties and increased water resistance. A similar improvement in performance characteristics has been observed by Sailaja [7] by modification via grafting with a hydrophobic polymer. However, a blend of LDPE with polar lignocellulosic materials would not be compatible, hence a compatibilizer such as maleated polyethylenes were used [8]. Improved interfacial bonding led to better Izod impact strength and tensile properties. The effect of various silane coupling agents for sisal fiber reinforced polyethylene and rubber composites were compared by Abdelmouleh et al. [9]. Improved thermal properties of rice husk flour filled polyolefin composites have been obtained by using a compatibilizing agent by Kim et al. [10].

In order to utilize lignin, straw lignin/polymer blends were developed by Pucciariello et al. [11]. The modulus values were improved while elongation drastically reduced for these blends. Similar behaviour for lignin/polyolefin blends was observed by Alexy et al. [12]. In order to enhance the interfacial bonding between lignin and LDPE, one of the authors has grafted polymethyl methacrylate (PMMA) onto lignin apart from using an epoxy functionalized compatibilizer [13]. Both mechanical properties and thermal stability for these blends were improved. A triblock copolymer was

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used as a compatibilizer for polyethylene/wood flour composites by Oaksman et al. [14]. The improved adhesion was confirmed by electron microscopy for the fractured surfaces.

In this study, esterified lignin–LDPE composites have been prepared. Lignin has been esterified using phthalic anhydride prior to blending in order to enhance its hydrophobicity. In order to further enhance the interfacial bonding, maleic anhydride grafted LDPE (PE-g-MA) has been used as a compatibilizing agent for these composites. No such studies have been found in the literature so far.

2. Experimental

2.1. Materials

LDPE (grade 24FS040 with MFI 4 g (10 min) from IPCL, Vadodara, India) was used for blending with lignin (Sigma Aldrich, USA). Maleic anhydride, phthalic anhydride, pyridine and other chemicals have been obtained from S.d. Fine Chem., Bangalore, India.

2.2. Esterification of lignin

Esterification of lignin was done in order to prepare lignin phthalate. Lignin phthalate was prepared by reacting lignin (10 g) with phthalic anhydride (28 g) in presence of pyridine (90 ml). The reaction was carried out at 120 °C for 3 h with continuous stirring. The resultant product was then precipitated in dilute sulphuric acid. The precipitates were filtered and washed repeatedly with water. The products were characterized using Fourier transform infrared spectroscopy (FTIR) (Perkin–Elmer spectrum 1000).

2.3. Synthesis of compatibilizer

LDPE-g-maleic anhydride compatibilizer has been synthesized as described earlier [15]. Five grams of LDPE has added to boiling toluene under reflux along with an equal amount of maleic anhydride. Benzoyl peroxide initiator (0–15 g) was added to this solution. The refluxing was continued for 4 h. The cooled solution was slowly precipitated in methanol. The unreacted maleic anhydride was removed by repeatedly rinsing the grafted polymer with fresh methanol. The grafted polymer was further washed with acetone and dried grafted polymer was finely powdered in a ball mill.

2.4. Melt blending

Blends of LDPE, lignin phthalate, LDPE-g-maleic anhydride as compatibilizer were prepared in varied proportions (by weight) by melt mixing at 210 °C in a heated cup fitted with a spiked motor. Dumb-bell shaped specimens were then molded as per ASTM specifications into standard dies supplied with the Minimax molder (Custom Scientific Instruments New Jersey, USA, Model CS-83 MMX). The amount of compatibilizer was based on weight percent of filler (lignin phthalate) throughout the study.

2.5. Mechanical properties of the blend

A Minimax impact (Model CS-183T1079) and tensile tester (Model CS-183TTE) (Custom Scientific Instruments, NJ, USA) was used to measure (unnotched) relative impact strength (RIS) and

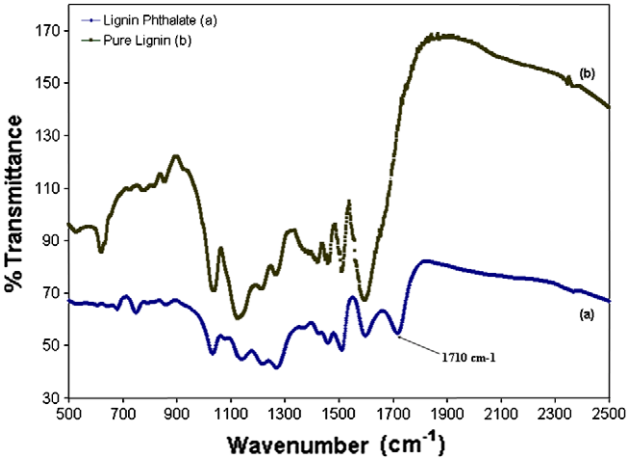

Fig. 1. FTIR spectrograph of the lignin phthalate and pure lignin.

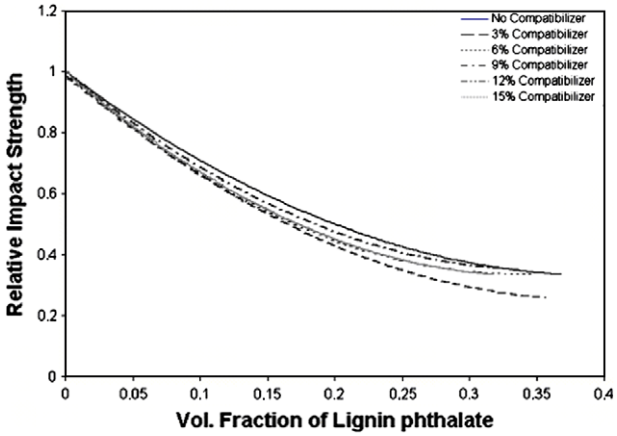

Fig. 2. Variation of relative impact strength with volume fraction of lignin phthalate.

Table 1
List of coefficients for Eq. (1).

Property (F)	Residual (R^2)	Standard error of estimate	Linear terms			Quadratic terms	
			a_0	a_1	a_2	a_3	a_4
RTS	0.81	0.0558	1.3093	−13.9479	−2.1498	1560.85	2.1127
RYM	0.61	0.3385	−0.8903	−6833.78	23.8833	65882.89	−37.3241
REB	0.93	0.0403	0.3282	10.4745	1.3295	−158.87	−4.1345
RIS	0.93	0.0392	0.2135	16.0172	2.2468	−249.89	−5.6247

	Interaction terms					
	a_5	a_6	a_7	a_8	a_9	a_{10}
RTS	9.3737	12649.40	635.41	18219.18	22789.93	−1263.15
RYM	76065.35	−512650.66	−268284.87	928671.19	156374.41	301498.09
REB	−4.8766	−310.55	−152.77	−380.26	9974.93	380.56
RIS	−22.3920	1079.46	−328.99	−692.25	−1607.90	745.81