Lignin-Filled Polyolefins

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ABSTRACT: Dry lignin powder was used as a filler in low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) up to 30% w/w. The tensile strength reduced for all polymers. Impact properties were almost unaffected for PP but reduced for the other two polymers, Use of five parts of ethylene acrylic acid copolymer (EAA) and 0.5 parts of titanate coupling agent improved mechanical properties considerably. The melt viscosity increased steadily with increasing amounts of lignin. Electrical properties showed improved electrical resistance. The color of the resulting compound could be evaluated only up to a 10% lignin level, beyond which the compounds became very dark. At lower concentrations, samples of HDPE showed a more reddish tinge, while at higher concentrations, all samples showed a green-blue tinge. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1321–1326, 1999

Key words: environment; polypropylene; high-density polyethylene; low-density polyethylene; lignin; filler

INTRODUCTION

Lignin, a major constituent of wood, is a polyphenolic compound. It binds the cellulosic fiber in a tree. Lignin is separated from cellulosic fibers in paper manufacturing. Its exact structure depends upon the conditions of the delignification process.¹ (Figure 1 shows a representative structure of lignin). Disposal of waste lignin is one of the major environmental problems. Considering phenolic nature of lignin, many chemical modifications have been studied. The lignin, being phenolic in nature, could be used for synthesis of phenolic resins.² Its hydroxyalkylated modification may be a source for some engineering plastics. Effect of lignin in styrene butadiene rubber has been evaluated by Falkehag, Sirianni, and others.³⁻⁶ By incorporation of lignin, an increase in thermal resistance of number of thermoplastics has been claimed by Bono et al.⁷ and Bubnova et

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al.⁸ The biodegradable nature of lignin-filled polyethylene has been claimed in another patent by Bono and Lambert.⁹

However, if lignin can be used as a filler, it would be commercially attractive. There are no systematic data on the mechanical, electrical, and rheological properties of lignin-filled polymers. Although lignin is a dark brown powder, the analysis of color of such compounds also has received almost no attention. Hence, such work would be useful.

MATERIALS USED

Commercial grades of low-density polyethylene (LDPE; FS 300, Indothene, supplied by IPCL, India), high-density polyethylene (HDPE; PM 4577F, supplied by NOCIL India), and polypropylene (PP; S3030 supplied by IPCL India) were used. The melt flow indices for the LDPE and HDPE were 5.6 and 0.4 g/10 min, respectively, at 190°C and a 2.16-kg load, while that for PP was 3 g/10 min at 230°C and a 2.16-kg load. Dry lignin

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Figure 1 Representative structure of lignin.

powder was supplied by M/s Padmjee Paper Mills Pvt. Ltd., India.

Ethylene acrylic acid copolymer (EAA; Primacore 1410 XT, Dow Chemicals, USA) and a titanate coupling agent (EB 1019, Mahesh Chemical Industries, India) were also of commercial grades.

EXPERIMENTAL WORK

Lignin was analyzed thermogravimetrically. It was predried at 140°C for 2 h before blending. LDPE, HDPE, or PP and a required amount of lignin were melt-blended using a HAAKE Rheomix 600 connected to a rheodrive. The mixing was achieved using a pair of counter-rotating universal rotors. LDPE was blended at a melt temperature of 170°C, while HDPE and PP were blended at 190°C. The melt-blended samples were compression-molded at a pressure of 150 kg/cm². The dumbbell-shaped specimen were punched out for testing mechanical properties. Similarly, the effect of five parts of EAA per 100 parts of filled polymer and also 0.5 parts of titanate coupling agent on the properties of filled polymer was studied. The tensile strength and percentage of elongation were determined using a Universal Testing Machine (R&D Electronics, Mumbai) at a crosshead speed of 50 mm/min. The izod impact was measured using an Avery Denison Impact Tester with stricking velocity of 3.41 m s. Melt rheology was measured at different temperatures (190, 210, and 230°C for HDPE and PP; 150, 170, and 190°C for LDPE) using HAAKE RT10, a rotational parallel plate viscometer, over a range of shear rates. The color strength and color analysis for molded samples was evaluated using a Milton Roy Colourmate HDS Spectrophotometer. Thermograms of the samples were determined using a differential scanning calorimeter (Perkin Elmer DSC7 series.)

RESULTS AND DISCUSSION

Lignin Analysis

The thermogravimetric analysis of lignin showed that the onset of loss in weight was at 235°C, and the percentage of loss was only 2% up to a temperature of 300°C. The elemental analysis was C = 60.5%, H = 5.7%, O = 33.13%, N = 0.67%, while the average particle size was $3-4 \mu m$.

Sr. No.	% Lignin	Tensile Strength (kg/cm ²)	Elongation at Break (%)	Tensile Strength of Blend of PP Tensile Strength of Virgin PP	Izod Impact (J/cm)
1	0	337	22	1.00	0.20
2	5	271	9	0.80	0.18
3	10	267	7	0.79	0.18
4	15	242	6	0.72	0.20
5	20	233	6	0.69	0.17
6	25	157	5	0.47	0.17
7	30	137	5	0.41	0.16
8	10^{a}	284	12	0.84	0.16
9	30^{a}	177	7	0.53	0.20
10	$10^{ m b}$	318	8	0.94	0.17
11	$30^{ m b}$	195	9	0.58	0.18
12	30°	171	7	0.51	0.1
13	$30^{\rm e}$	195	9	0.58	0.18

 Table I
 Mechanical Properties of Lignin-Polypropylene Blends

^a With 5-phr EAA.

 $^{\rm b}$ With 0.5-phr titanate coupling agent.

° With 10-phr EAA.

^e With 5-phr EAA and 0.5-phr titanate coupling agent.

Mechanical Properties

The variation of tensile strength and the percentage of elongation with the percentage of lignin is shown in Tables I-III. The tensile strength decreased quite substantially for all the three polymers. The extent of decrease was less for LDPE. The impact strength of PP decreased only marginally, while that of LDPE and HDPE reduced considerably. The decrease in tensile properties may indicate poor compatibility or interaction between lignin and the matrix polymer. The tables also give the ratio of tensile strength of filled polymer to unfilled virgin polymer. The percentage of reduction in the tensile strength of HDPE and PP appears to be similar, while the reduction for LDPE was less. The reduction in impact properties of PP was least (only about 10-15%), while that for HDPE and LDPE was comparable. The electron donor pendant methyl group in polypropylene and the electron-accepting cresolic nature of lignin may show some kind of interaction; hence, the properties of PP may not be affected as much as those of LDPE and HDPE.

The use of EAA and a titanate coupling agent improved both tensile strength as well as the percentage of elongation substantially. The EAA and titanate seem to have improved the bonding between the polymer and the lignin. The improvement in mechanical properties was more when level of lignin was 10% at a given loading of EAA or coupling agent. Hence, the effect of doubling the concentration of the two was evaluated. It is clearly seen that the improvement was only marginal, even if EAA loading increased from 5 to 10 phr. The combined action of EAA and the coupling agent also was only marginally better.

Electrical and Thermal Properties

The break down voltage (BDV) increased substantially with addition of lignin, indicating improved electrical resistance for all the three matrix polymers (Table IV). The increase was more for LDPE and PP while less for HDPE. Addition of EAA or titanate improved the resistance still further. The structure of lignin is very complicated, as shown in Figure 1. The bulky, threedimensional structure of lignin and the absence of unsaturation can lead to reduced mobility of the segments of matrix polymer molecule, as well as the lignin itself. Such a restriction will increase the electrical resistance. The poor electrical conductivity of wood could be partly due to structure of lignin.

The heat deflection temperature increased by 5°C for lignin-filled PP, but that for filled HDPE and LDPE remained unaffected (Table V). Differential scanning calorimetry (DSC) data did not

Sr. No.	% Lignin	Tensile Strength (kg/cm ²)	Elongation at Break (%)	Tensile Strength of Virgin LDPE	Tensile Strength of Blend of LDPE Izod Impact (J/cm)
1	0	110	255	1.00	2.20
2	5	96	47	0.87	1.00
3	10	91	44	0.83	0.85
4	15	84	35	0.76	0.65
5	20	76	23	0.69	0.60
6	25	69	18	0.63	0.60
7	30	67	15	0.61	0.55
8	10^{a}	95	47	0.86	1.80
9	30^{a}	74	18	0.67	0.60
10	10^{b}	95	52	0.86	1.70
11	30^{b}	82	17	0.75	0.60
12	30°	76	18	0.69	0.65
13	$30^{\rm d}$	82	17	0.75	0.65
14	$30^{\rm e}$	83	19	0.75	0.75

Table II Mechanical Properties of Lignin-Low Density Polyethylene Blend

^a With 5-phr EAA.
^b With 0.5-phr titanate coupling agent.
^c With 10-phr EAA.
^d With 1-phr titanate coupling agent.
^e With 5-phr EAA and 0.5-phr titanate coupling agent.

Sr. No.	% Lignin	Tensile Strength (kg/cm ²)	Elongation at Break (%)	Tensile Strength of Unfilled HDPE	Tensile Strength of Blend of HDPE Izod Impact (J/cm)
1	0	323	601	1.00	1.90
2	5	211	283	0.65	0.70
3	10	201	198	0.62	0.60
4	15	184	143	0.57	0.60
5	20	169	94	0.52	0.55
6	25	160	61	0.50	0.60
7	30	153	53	0.47	0.60
8	10^{a}	267	315	0.83	0.73
9	30^{a}	180	60	0.56	0.60
10	$10^{ m b}$	276	361	0.85	1.50
11	30^{b}	186	63	0.58	0.63
12	30°	184	69	0.57	0.65
13	30^{d}	180	59	0.56	0.65
14	30^{e}	189	65	0.59	0.70

Table III Mechanical Properties of Lignin-High-Density Polyethylene Blends

^a With 5-phr EAA.
^b With 0.5-phr titanate coupling agent.
^c With 10-phr EAA.
^d With 1-phr titanate coupling agent.
^e With 5-phr EAA and 0.5-phr titanate coupling agent.

9		Break Down Voltage (kV mm)			
Sr. No.	% Lignin	PP	LDPE	HDPE	
1	0	12.50	14.28	11.11	
2	5	14.75	15.89	12.91	
3	10	15.22	16.00	13.33	
4	20	15.69	18.58	14.28	
5	30	15.00	17.69	10.00	
6	10^{a}	16.21	17.14	16.66	
7	30^{a}	15.40	17.78	14.45	
10	10^{b}	15.00	15.04	15.28	
11	$30^{ m b}$	15.55	17.98	14.51	

Table IVElectrical Properties of Lignin-FilledPolymers

^a With 5-phr EAA.

^b With 0.5-phr titanate coupling agent.

show any influence of lignin on the onset or peak melting characteristics of the base polymer.

Color Analysis

The color analysis of molded samples could be carried out up to 10% concentration of lignin only. Table VI shows the difference in the L, a, and b values of lignin-filled samples. It is clear from the table that all the samples tend to become darker as the lignin loading increased; and by 10% lignin loading, the samples became completely dark. The ΔL became increasingly more negative with increased concentration of lignin. Even at a 1% lignin level, the color was substantially dark

Table VHeat Deflection Temperature ofLignin-Filled Polymers

		Heat Deflection Temperature $(^{\circ}C)$			
Sr.	%				
No.	Lignin	PP	LDPE	HDPE	
1	0	50	_	30	
2	5	50	_	30	
3	10	50	_	30	
4	20	52	_	30	
5	30	53	_	30 - 32	
6	10^{a}	55	_	30 - 32	
7	30^{a}	54	_	30 - 32	
10	$10^{ m b}$	55	_	30 - 32	
11	30^{b}	55	—	30 - 32	

^a With 5-phr EAA.

^b With 0.5 titanate coupling agent.

Table VIDifference in L, a, and b Values ofLignin-Filled Polyolefins

Sr —	0%			
No.	Lignin	ΔL	Δa	Δb
	F	Polypropylene		
1	0	0	0	0
2	1	-42.79	2.39	-6.45
3	2	-44.74	1.56	-7.39
4	5	-45.01	0.16	-8.47
5	10	-45.96	0.08	-8.76
	Low-de	ensity polyeth	nylene	
6	0	0	0	0
7	1	-35.24	1.18	-8.06
8	2	-37.44	-1.52	-10.87
9	5	-38.27	-2.34	-11.47
10	10	-37.85	-2.50	-11.61
	High-d	ensity polyet	hylene	
11	0	0	0	0
12	1	-44.74	3.56	-5.76
13	2	-45.47	3.07	-6.19
14	5	-47.14	2.49	-7.02
15	10	47.24	2.48	-7.25

(large ΔL values). At a given loading, LDPE was less dark. At lower concentrations, samples of HDPE showed more a reddish tinge, while at higher concentration, all the samples showed a green-blue tinge.



Figure 2 Effect of lignin loading on rheological properties of polypropylene: (\bigcirc) PP; (\triangle) 10%, (\diamondsuit) 20%, and (\square) 30% lignin-filled PP.

Rheology

The melt viscosity increased as the percentage of lignin increased. The increase in viscosity of LDPE was more than that for HDPE and PP. The increase in viscosity remained unaffected, even when EAA or titanate were incorporated. All the samples showed a presence of zero shear viscosity. Figures 2 and 3 show a typical variation of viscosity for 20% ligninfilled LDPE, HDPE, and PP. The zero shear viscosity increased almost linearly with the percentage of lignin. The difference in the viscosity of filled polymers and virgin polymer was less at high shear rates, indicating a higher shear thinning behavior for lignin-filled polymers. The effect of lignin on the zero shear viscosity at 190°C of all the three polymers is given in Table VII. Detailed analysis of the viscous behavior of lignin-filled polymers is presented by Kharade and Kale.¹⁰ They have used the Ellis model to describe the flow behavior of ligninfilled PP, LDPE, and PP. The activation energy for the variation of zero shear viscosity with temperature was the same for neat as well as lignin-filled polymers.



Figure 3 Comparison of rheological properties of 20% lignin-filled LDPE and HDPE: (\bigcirc) LDPE; (\square) 20% lignin-filled LDPE; (\triangle) HDPE; (\diamond) 20% lignin-filled HDPE.

Table VII	Variation	of Zero	Shear	Viscosity	of
Lignin-Fil	led Polyme	ers			

~		Zero Shear Viscosity (Pa S)			
Sr. No.	% Lignin	PP	LDPE	HDPE	
1	0	$3.8 imes10^3$	$3.0 imes10^3$	$5.0 imes10^4$	
2	5	$3.9 imes10^3$	$3.5 imes10^3$	$6.1 imes10^4$	
3	10	$4.2 imes10^3$	$3.8 imes10^3$	$6.8 imes10^4$	
4	15	$4.9 imes10^3$	$4.2 imes10^3$	$8.9 imes10^4$	
5	20	$5.2 imes10^3$	$4.8 imes10^3$	$1.0 imes 10^5$	
6	25	$5.8 imes10^3$	$5.1 imes10^3$	$1.3 imes10^5$	
7	30	$6.2 imes10^3$	$6.0 imes10^3$	$1.5 imes10^5$	

CONCLUSIONS

The lignin-filled polyolefins showed considerably higher electrical resistance. The impact strength of PP decreased only marginally, even when lignin loading was as high as 30%. Use of EAA or titanate titanate coupling agent improved the mechanical properties of lignin-filled polyolefins considerably.

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