

# Modification of Lignin–Polyethylene Blends with High Lignin Content Using Ethylene–Vinylacetate Copolymer as Modifier

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**ABSTRACT:** Blending of polyethylene with lignin in concentrations > 20 wt % yielded blends with relatively low mechanical properties. A new method, based on modification of polyethylene with ethylene–vinylacetate (EVA) copolymer, was developed for the preparation of polyethylene blends containing about 30 wt % lignin with acceptable strength properties. The addition of 10 wt % EVA caused an increase of tensile strength about twice and elongation at break about 13 times compared to those of the corresponding nonmodified samples. The optimization of lignin–poly-

ethylene–EVA blend composition was based on a regression equation, which was obtained as output from an experimental design. The prepared composite material with 33.6 wt % lignin showed acceptable processing and mechanical properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1855–1860, 2004

**Key words:** lignin; blends; modification; optimization; mechanical properties

## INTRODUCTION

During the last few years several reported studies and patents have focused on the use of lignin as a natural filler in various polymer matrices. A U.S. patent<sup>1</sup> was granted for lignin applications of blends based on ethylene copolymers as polymer matrix. Košíková et al.<sup>2–4</sup> described the modification of polypropylene by sulfur-free lignin and its influence on mechanical, physicochemical, and surface properties as well as on the degradation of lignin–polypropylene films. Feldman et al.<sup>5</sup> prepared lignin–polyurethane blends and determined their morphology. Various polyolefins filled by lignin and ethylene–acrylic acid copolymer were studied by Sastry et al.<sup>6</sup> The effects of blending lignin with polyethylene and polypropylene on the processing stability, light stability, and long-term heat stability, as well as mechanical properties of blends with different lignin content, were described in our previous work.<sup>7</sup> It was revealed that the tensile strength of polymers continually decreases with increasing lignin content.

The objective of the present study was to improve the mechanical properties of polyethylene containing

a high amount of lignin by the addition of ethylene–vinylacetate copolymers.

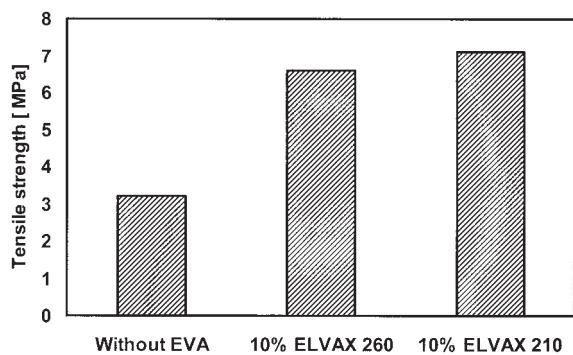
## EXPERIMENTAL

Low-density polyethylene (LDPE), with a melt flow index (MFI) ranging from 1.7 to 2.3 g/10 min (BRALEN FB 2-30 Slovnaft, Bratislava, Slovakia), was used as the polymer matrix. Prehydrolysis lignin powder ( $M_w = 2000$ ) was obtained by fractionation of beech wood prehydrolyzate at the Institute of Chemistry, Slovak Academy of Sciences (Bratislava, Slovakia). EVA copolymers containing 28% of vinylacetate units with MFI values of 6 and 400 g/10 min (ELVAX 260 and ELVAX 210, respectively; DuPont, Wilmington, DE) were used as modifiers. An amide of erucic acid (Loxamide E, Henkel Waschmittel GmbH, Düsseldorf, Germany) was used as a processing aid.

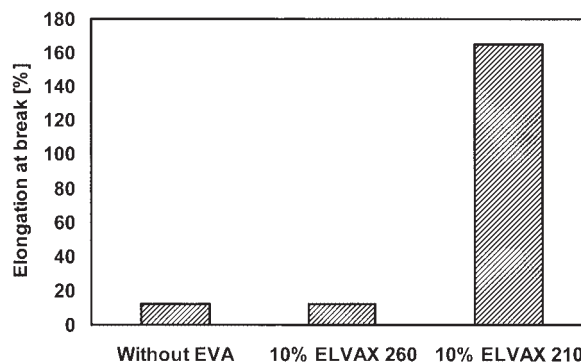
All samples were prepared by double regranulation of mechanical dry blends using a single-screw extruder (Brabender) at the following processing parameters:

Screw diameter	19 mm
L/D ratio	25
Compression ratio	1 : 4
Temperature profile	150–160–180–170°C (from filling to head)
Screw operation speed	50 min <sup>-1</sup>

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**Figure 1** Influence of EVA copolymers on tensile strength of blends containing 27 wt % of lignin in polyethylene Bralen FB 2-30 matrix.



**Figure 2** Influence of EVA copolymers on elongation at break of blends containing 27 wt % of lignin in polyethylene Bralen FB 2-30 matrix.

The MFI was measured using an M201 plastometer (die diameter = 2 mm) at 190°C. Preheating time was 4 min and loading was 21.18 N. For mechanical property measurements, tapes were extruded under the preceding conditions, when the head for tapes was used. The die for tape extrusion had cross-sectional dimensions of 20 × 1 mm. Tensile strength and elongation at break were measured using a Monsanto 10 tensometer (Monsanto, St. Louis, MO), according to ISO 527, using type 5A testing pieces and a crosshead speed of 50 mm/min.

## RESULTS AND DISCUSSION

The possibility of lignin–polyethylene blend modification was examined using ethylene–vinylacetate (EVA) copolymers to increase the mechanical properties. From Figures 1 and 2 it can be seen that the polyethylene blend containing 27 wt % lignin exhibits low tensile strength and extremely low elongation at break. This blend was modified by application of two EVA copolymers containing 28 wt % vinylacetate, with MFI values of 6 and 400 g/10 min, respectively. The addition of both EVA copolymers in the amount of 10 wt % increased the tensile properties by more than twice (Fig. 1). Similarly, the modified lignin–polyethylene blend achieved substantially higher values of elongation of break (Fig. 2) because of the presence of ELVAX 210, compared with that of both the nonmodified polymer sample and the sample with ELVAX 260. The EVA copolymer with higher MFI

(ELVAX 210) was a more efficient modifier for the polyethylene–lignin blend. Both tensile strength and elongation at break increment of the tested lignin–polyethylene blends was higher in the case of modification by EVA with higher MFI.

In attempts to significantly improve the strength properties of the composite lignin–polyethylene blends by addition of EVA copolymer, the optimization of composition was calculated for polyethylene–EVA blends with high lignin content. The weight ratios of the individual blend components were chosen as the factors for experimental design, according to Table I.

Based on experimental design condition (Table I) a series of various blends, with compositions detailed in Table II, was prepared. All measured parameters for each blend are listed in Table III.

The measured values for each parameter were processed according to design of experiment (DOE) theory using the computer program STATIS, written by the authors in MS Excel Visual Basic. Output from the program was in the form of full regression and statistical analysis, where the analysis of variance (ANOVA) method was used. All statistical tests were carried out at a probability level of 95%. For each parameter the following type of regression equation was obtained:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

**TABLE I**  
Conditions of Experimental Design

Factor	Weight ratio	−1.682	−1	0	1	1.682
$x_1$	EVA/PE	0.0738	0.1649	0.2987	0.4324	0.5236
$x_2$	PLE/(EVA + PE)	0.1784	0.2529	0.3622	0.4715	0.5461
$x_3$	LOX/(EVA + PE + PLE)	0.0030	0.0054	0.0091	0.0128	0.0153

<sup>a</sup> EVA = Elvax 210; PE = Bralen FB 2–30; PLE = lignin; and LOX = Loxamid E.

TABLE II  
Composition of the Blends of Experimental Design

Trial no.	Sample no.	Factor $x_1$	Factor $x_2$	Factor $x_3$	EVA (wt %)	PE (wt %)	PLE (wt %)	LOX (wt %)
1	G/185	0.16	0.25	0.005	11.2	68.1	20.1	0.5
2	G/186	0.43	0.25	0.005	24.0	55.4	20.1	0.5
3	G/187	0.16	0.47	0.005	9.6	58.0	31.9	0.5
4	G/188	0.43	0.47	0.005	20.4	47.2	31.9	0.5
5	G/189	0.16	0.25	0.013	11.2	67.6	19.9	1.3
6	G/190	0.43	0.25	0.013	23.8	55.0	19.9	1.3
7	G/191	0.16	0.47	0.013	9.5	57.6	31.6	1.3
8	G/192	0.43	0.47	0.013	20.3	46.8	31.6	1.3
9	G/193	0.07	0.36	0.009	5.0	67.7	26.3	0.9
10	G/194	0.52	0.36	0.009	25.0	47.7	26.3	0.9
11	G/195	0.29	0.18	0.009	19.3	64.8	15.0	0.9
12	G/196	0.29	0.55	0.009	14.7	49.4	35.0	0.9
13	G/197	0.29	0.36	0.003	16.8	56.4	26.5	0.3
14	G/198	0.29	0.36	0.015	16.6	55.7	26.2	1.5
15	G/199	0.29	0.36	0.009	16.7	56.0	26.3	0.9
16	G/200	0.29	0.36	0.009	16.7	56.0	26.3	0.9
17	G/201	0.29	0.36	0.009	16.7	56.0	26.3	0.9
18	G/202	0.29	0.36	0.009	16.7	56.0	26.3	0.9
19	G/203	0.29	0.36	0.009	16.7	56.0	26.3	0.9
20	G/204	0.29	0.36	0.009	16.7	56.0	26.3	0.9

where  $y$  is an output parameter;  $x_1$ ,  $x_2$ , and  $x_3$  are levels of factors in coded coordinates; and  $b_0$ – $b_{33}$  are regression coefficients.

Results of ANOVA for all three measured parameters are listed in Tables IV, V, and VI and values of regression coefficients are listed in Table VII.

The dependency of MFI and tensile strength on factors  $x_1$  and  $x_2$  at constant level of factor  $x_3$  is shown in Figures 3 and 4, respectively, in response surface form.

TABLE III  
Measured Parameters

Sample no.	MFI (g/10 min)	Tensile strength (MPa)	Elongation at break (%)
G/185	8.16	9.76	338
G/186	12.89	6.98	307
G/187	3.1	5.16	32
G/188	11.26	5.5	177
G/189	3.78	9.04	368
G/190	3.06	6.74	283
G/191	14.9	4.68	72
G/192	22.7	5.1	40
G/193	5.53	6.62	227
G/194	12.58	5.76	27
G/195	13.75	8.58	329
G/196	16.76	4.22	33
G/197	11.39	8	310
G/198	14.83	6.74	171
G/199	16.03	6.5	216
G/200	17.74	6.94	242
G/201	18.31	6.44	230
G/202	22.12	5.94	152
G/203	16.85	5.64	123
G/204	16.21	6.54	226

An increase of the ratios of EVA/PE as well as PLE/(EVA + PE) caused an increase of MFI according to the response surface. According to the EVA/PE axis MFI shows a maximum, which can be observed on the response surface (Fig. 3) as well as according to the negative value of coefficient  $b_{11}$  (see Table VII). It can be seen that MFI can vary in dependency on blend composition from very low values (<1 g/10 min) up to about 20 g/10 min.

The results summarized in Figure 4 show that tensile strength decreases if the lignin concentration increases [increasing of PLE/(PE + EVA) ratio]. Increase

TABLE IV  
Results of ANOVA for Melt Flow Index (MFI)<sup>a</sup>

Parameter	SS	$f$	$s^2$	$F$	$F_{crit}$
S1	150.8	3	50.3	9.9	5.41
S2	440.4	6	73.4	14.4	4.95
SR	58.0	10	5.8	—	—
SE	25.5	2	5.1	—	—
SLF	32.5	5	6.5	1.3	5.05
Standard deviations					
$s_E$	2.3				
$s_{LF}$	2.6				
$s_{LF01}$	6.6				

<sup>a</sup> S1, evaluation for linear part of regression equation; S2, evaluation for nonlinear part of regression equation; SR, evaluation for residuum; SE, evaluation for experimental error; SLF, lack of fit evaluation; SS, square sum;  $f$ , degrees of freedom;  $s^2$ , variance;  $F$ , value of  $F$ -test;  $F_{crit}$ , critical value for  $F$ -test at 95% level of probability;  $s_E$ , standard deviation for experimental error;  $s_{LF}$ , lack of fit standard deviation for full equation;  $s_{LF01}$ , lack of fit standard deviation for linear part of equation.

**TABLE V**  
Results of ANOVA for Tensile Strength<sup>a</sup>

Parameter	SS	<i>f</i>	<i>s</i> <sup>2</sup>	<i>F</i>	<i>F</i> <sub>crit</sub>
S1	31.2	3	10.4	47.9	5.41
S2	6.3	6	1.0	4.8	4.95
SR	1.6	10	0.2	—	—
SE	1.1	5	0.2	—	—
SLF	0.5	5	0.1	0.5	5.05
Standard deviations					
<i>s</i> <sub>E</sub>	0.5				
<i>s</i> <sub>LF</sub>	0.3				
<i>s</i> <sub>LF01</sub>	0.8				

<sup>a</sup> Terms defined as in Table IV.

of EVA content in the polymer matrix (increasing of EVA/PE) can significantly eliminate this negative effect, mainly at high concentrations of lignin. The mutual interaction is also confirmed in this case between EVA and lignin by significant interaction coefficient *b*<sub>12</sub> (see Table VII).

Dependency of elongation at break was not investigated because it was found that this parameter depends only on factor *x*<sub>2</sub> (i.e., only on lignin content). Statistical and regression analysis showed that elongation at break continuously decreases with increasing lignin concentration.

**TABLE VI**  
Results of ANOVA for Elongation at Break<sup>a</sup>

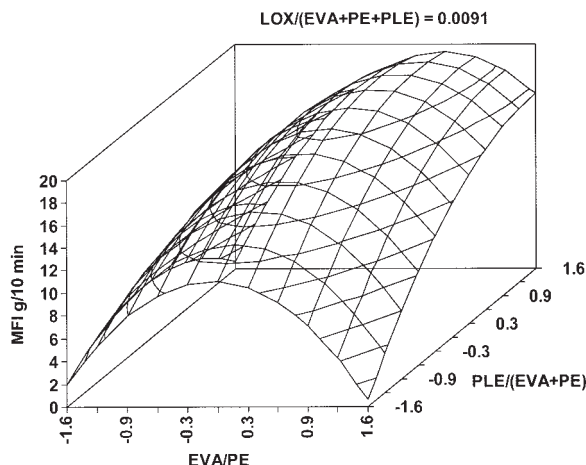
Parameter	SS	<i>f</i>	<i>s</i> <sup>2</sup>	<i>F</i>	<i>F</i> <sub>crit</sub>
S1	174994.4	3	58331.5	24.7	5.41
S2	27491.3	6	4581.9	1.9	4.95
SR	33344.8	10	3334.5	—	—
SE	11808.8	5	2361.8	—	—
SLF	215356.0	5	4307.2	1.8	5.05
Standard deviations					
<i>s</i> <sub>E</sub>	48.6				
<i>s</i> <sub>LF</sub>	65.6				
<i>s</i> <sub>LF01</sub>	66.8				

<sup>a</sup> Terms defined as in Table IV.

**TABLE VII**  
Regression Coefficient Values for Measured Properties of Prepared Blends and Tapes<sup>a</sup>

Coefficient	MFI	Tensile strength	Elongation at break
<i>b</i> <sub>0</sub>	<b>17.970</b>	<b>6.335</b>	<b>197.50</b>
<i>b</i> <sub>1</sub>	<b>2.331</b>	<b>-0.422</b>	<b>-24.847</b>
<i>b</i> <sub>2</sub>	<b>2.134</b>	<b>-1.422</b>	<b>-107.87</b>
<i>b</i> <sub>3</sub>	1.030	-0.290	-23.782
<i>b</i> <sub>11</sub>	<b>-3.561</b>	-0.062	-20.908
<i>b</i> <sub>12</sub>	1.494	<b>0.730</b>	28.625
<i>b</i> <sub>13</sub>	-0.726	0.070	-28.875
<i>b</i> <sub>22</sub>	-1.367	0.012	-1.798
<i>b</i> <sub>23</sub>	<b>4.681</b>	0.010	-12.875
<i>b</i> <sub>33</sub>	<b>-2.206</b>	<b>0.356</b>	19.258

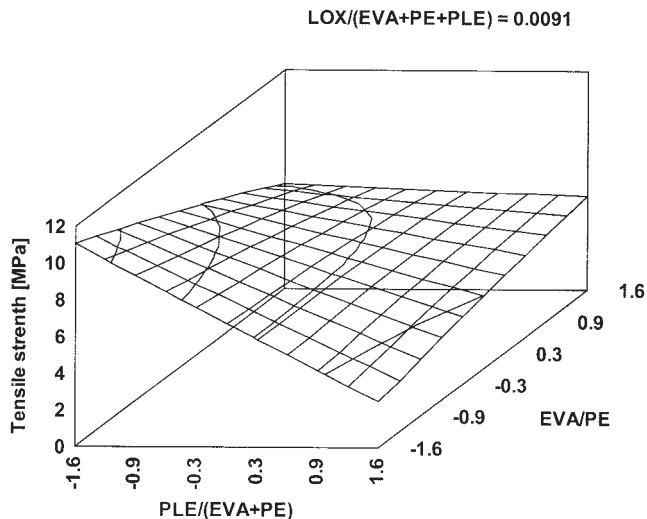
<sup>a</sup> Statistically significant coefficients are in bold.



**Figure 3** Response surface of melt flow index in dependency on factor *x*<sub>1</sub> (weight ratio EVA/PE) and factor *x*<sub>2</sub> (weight ratio PLE/(EVA + PE)) in coded coordinates at constant factor *x*<sub>3</sub> (LOX/(EVA + PE + PLE)).

Based on the ANOVA (Tables IV–VI), the sufficient accuracy of all regression equations was confirmed with respect to experimental error. However, it must be noted, that—mainly in cases of MFI and elongation at break—both experimental and regression standard deviations together gave relatively high values and thus a higher declination can be expected between the real value of both parameters and their equivalents calculated according to regression equations.

All regression equations were used to calculate the composition of blends with respect to required properties. The subprogram SOLVER from MS EXCEL was



**Figure 4** Response surface of tensile strength in dependency on factor *x*<sub>1</sub> (weight ratio EVA/PE) and factor *x*<sub>2</sub> (weight ratio PLE/(EVA + PE)) in coded coordinates at constant factor *x*<sub>3</sub> (LOX/(EVA + PE + PLE)).

**TABLE VIII**  
**Optimization Computation Input and Output**

Constraints	
Parameter	Required value
Tensile strength	minimum 6 MPa
Elongation at break	minimum 200%
Melt flow index	minimum 2 g/10 min
Lignin content	as high as possible
Outputs	
Parameter	Output value
$x_1$	0.78
$x_2$	1.34
$x_3$	-1.68
Bralen FB 2-30 content	47.2 wt %
ELVAX 210 content	18.9 wt %
Lignin content	33.6 wt %
Loxamid E content	0.3 wt %
Calculated properties	
Property	Value
Tensile strength	6.2 MPa
Elongation at break	209%
Melt flow index	20.9 g/10 min

used for optimization computation. The requirements for composition and properties of the blends were as follows (all requirements are given with respect to experimental and regression standard deviations):

Lignin content	as much as possible
Melt flow index	minimum 2 g/ 10 min
Tensile strength	minimum 6 MPa
Elongation at break	minimum 200%

The main purpose of this optimization was to obtain a composition with a lignin content as high as possible, simultaneously with retaining base processing and mechanical properties at acceptable levels. The results of optimization computation are presented in Table VIII.

The blend with composition calculated according to Table VIII was prepared with the same experimental technique as that of all the samples in experimental design. The real measured values of this sample, designated as G205, were compared with calculated values according to optimization computations as well as with values of the best result before optimization (blend designated as G177 with 27 wt % lignin content and 10.9 wt % of Elvax 210 without Loxamid E) and the blend without modifier, designated as G180. The comparison is shown in Table IX.

Results presented in Table IX show good agreement between calculated values and actual measured values for blend G205. Differences in all parameters are lower than, or comparable with, corresponding standard deviations (see Table VIII). When blends G205 and G177 are compared, slight differences in tensile strength and elongation at break are observed, although the optimized blend G205 contains 6.6 wt % higher content of lignin. The MFI for the optimized blend G205 is significantly higher. Both samples with modifier (G177 and G205) showed much better elongation at break and also significantly better tensile strength than those of sample G180 without modifier. The prepared blend G205 was tested for film-blowing processing in laboratory scale with a good result; a compact film with 0.080 mm thickness was prepared.

## CONCLUSIONS

The lignin byproduct of wood processing can be successfully used as a filler for polyethylene. Modification of blends with EVA copolymers significantly improved both the processing and mechanical properties of final materials containing lignin in amounts > 30%. In the present work optimization was made to determine the best concentration ratios between polyethylene matrix, EVA copolymer, lignin, and processing aid at a lignin content that was as high as possible. The main result of our work was the evaluation of mutual effects in the system using DOE methodology and calculation of optimal com-

**TABLE IX**  
**Comparison of Measured Values of Blend G205 with Calculated Values in Optimizing Process as Well as with Samples G177 and G180**

Parameter	Blend G205		Blend G177	Blend G180
	Calculated value	Measured value		
Tensile strength, MPa	6.2	5.2	7.1	3.2
Elongation at break, %	209	141	165	12
Melt flow index, g/10 min	20.9	19.0	8.8	7.4
Lignin content, wt %	33.6	—	27	27
Elvax 210 content, wt %	18.9	—	10.9	—
Loxamid E content, wt %	0.3	—	0	—

position of blend. Optimizing computation was done based on DOE regression equations. Composition of blend with 33.6 wt % of lignin was calculated. The experimental verification shows good agreement between the calculated and measured values. The calculated blend showed improvement in mechanical properties of the polyethylene–lignin material simultaneously with increasing lignin content in the blend up to 33.6 wt % level. The obtained results provide ample confirmation for use of lignin in composite materials with improved compatibility with natural environment.

## References

1. Bono, P.; Lambert, C. U.S. Pat. 5,321,065 (1994).
2. Košíková, B.; Demianová, V.; Kacuráková, M. *J Appl Polym Sci* 1993, 47, 1065.
3. Košíková, B.; Demianová, V.; Mikulášová, M. *Wood Res* 1994, 3, 15.
4. Košíková, B.; Revajová, A.; Demianová, V. *Eur Polym Mater* 1995, 31, 953.
5. Feldman, D.; Lacasse, M. A. *Mater Res Soc Symp Proc* 1989, 153, 193.
6. Sastry, P. K.; Saryanarayana, D.; Rao, D. V. *J Appl Polym Sci* 1998, 70, 2251.
7. Alexy, P.; Košíková, B.; Podstránska, G. *Polymer* 2000, 41, 4901.