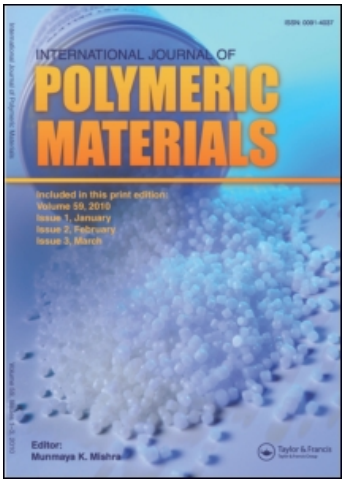


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# Wood Flour/Polypropylene Composites: Influence of Maleated Polypropylene and Process and Composition Variables on Mechanical Properties

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# Wood Flour/Polypropylene Composites: Influence of Maleated Polypropylene and Process and Composition Variables on Mechanical Properties

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The mechanical properties of wood flour/polypropylene composites may be improved by using coupling agents to enhance the bonding between filler and matrix. We used a two-level, full-factorial experiment to examine the effectiveness of a commercially available additive, Epolene E-43, on strength (tensile, flexural, and cantilever-beam), modulus, impact energy, density, and melt viscosity of composites. The effect of Epolene E-43 was studied alone and in combination with three other variables: the weight ratio of wood flour to total polymer in the composites (45/55 or 55/45), size of wood flour particles (nominal 20 or 40 mesh), and extruder residence time (one or three extrusions). Of all the variables, Epolene E-43 had the greatest effect on strength. This effect was somewhat enhanced by using the 40-mesh wood flour and three extrusions; for this combination of variables, Epolene E-43 caused a 30 percent increase in strength. The combination of Epolene E-43 with a 55/45 wood flour/polymer ratio and 40-mesh wood flour resulted in the largest values of flexural and cantilever-beam modulus. Addition of Epolene E-43 slightly decreased notched impact energy but possibly increased unnotched impact energy. None of the variables had a significant effect on melt viscosity. Average wood flour particle size was decreased by processing, particularly in the presence of Epolene E-43. Overall, these findings indicate that Epolene E-43 exerts some degree of coupling action, which results in improvements in mechanical properties that have practical value. The higher cost of Epolene E-43 can be compensated by increasing the ratio of wood flour to polypropylene.
KEYWORDS Polypropylene, wood flour, filler, composite, coupling agent, maleated polypropylene, mechanical properties, extrusion

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## INTRODUCTION

In recent years, interest has grown in composites made from wood flour or wood fiber in thermoplastic matrices, particularly for low cost/high volume applications. This development has occurred because wood-derived fillers have several advantages compared to inorganic fillers: lower density, greater deformability (which results in lower filler damage during processing), less abrasiveness to equipment, and lower cost. Moreover, wood-derived fillers are derived from a renewable resource.

One product of particular interest is the thermoformable, extruded panel, which contains approximately equal parts by weight of wood flour and isotactic polypropylene. A current major application is for the interior panels of automobiles. Typically, the dispersion of 50 percent wood flour by weight in polypropylene by way of melt processing causes an increase in certain properties of the panel (relative to neat polymer): a 15 to 20 percent increase in density, $\geq$100 percent increase in modulus, and 35°C increase in heat distortion temperature. On the other hand, rupture strength may be decreased by as much as 25 percent, although it is sometimes increased; unnotched impact energy may drop to a small fraction of the value of neat polymer; and melt flow is greatly decreased.



For many applications, losses in strength, impact energy, and flow-related processing properties of wood-filled systems need to be moderated or eliminated while improvements in other properties are retained. Efforts to do so have centered on the use of coupling agents to enhance the inherently poor attraction between polar wood and nonpolar polypropylene. Dalvag and coworkers recently summarized the approaches to this problem.[1] One promising coupling agent is maleated polypropylene (MAPP), that is, polypropylene that has been reacted with maleic anhydride by free radical grafting reactions. The reaction product apparently contains succinic anhydride moieties, which are located within the polypropylene chains or at chain ends.[2,3] With wood filler, the anhydride groups are presumably attracted by (possibly reacted with) the wood, whereas the polypropylene segments provide miscibility with the matrix polypropylene. In fact, Kishi and coworkers demonstrated that xylene extraction of the polymer from such systems leaves a filler residue of higher weight than that remaining from a comparable system without maleated polymer, and the higher-weight residue exhibits infrared peaks expected for anhydride.[4] Others report that wood is esterified by dicarboxylic anhydrides in the absence of solvent at elevated temperatures.[5] The viscosity increase (perhaps twofold?) observed on adding one type of MAPP is also consistent with improved bonding between filler and matrix polymer.[1]

Table I presents property data taken from available reports on various MAPP/matrix polymer/lignocellulosic filler combinations. The systems encompass three different MAPP types, four fillers, three polymer types, as well as different percentages of components. Where comparisons can be made, the observed effects of substituting maleated polymer for nonmaleated polymer differ in both magnitude and sign among the different studies; for example, tensile

TABLE I

Reported properties of polyolefin/lignocellulosic composite containing maleated polypropylene[a]

| Composite[b,c] | Bending rupture stress (MPa) | Bending modulus (GPa) | Tensile rupture stress (MPa) | Tensile maximum stress (MPa) | Tensile rupture strain (percent) | Tensile modulus (GPa) | Impact energy (J/m) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Notched (Izod) | Unnotched (Charpy) |
| 49 Kraft pulp/ 50 PP/1 MAPP-1 (Ref. 8) | 78(0.9) | 5.5(NA) | 46(0.9) | — | — | 5.8(NA) | 26(NA) | — |
| 29 WF/70 EPP/ 1 MAPP-2 (Ref. 1) | — | — | — | 31(1.2) | 6(1.9) | — | — | 43(1.5) |
| 29 CF/70 EPP/ 1 MAPP-2 (Ref. 1) | — | — | — | 29(1.7) | 8(2.0) | — | — | 85(2.0) |
| 50 RGP/40 PP/ 10 MAPP-3 (Ref. 4) | — | — | — | 17(1.4) | 1.0(1.2) | 1.6(1.0) | — | — |
| 50 RGP/ 50 MAPP-3 (Ref. 4) | — | — | — | 28(2.3) | 2.9(3.5) | 1.7(1.1) | — | |
| 50 RGP/49 PP/ 1 MAPP-4 (Ref. 6) | — | — | — | 42(3.6) | — | 2.3(1.9) | — | — |
| 53/WF 46 PP/ 1 MAPP-1 (Ref. 7) | — | 4.4(1.3) | 3.2(1.6) | — | — | — | 32(0.9) | — |

[a] Measured values for composites. Numbers in parentheses are magnitudes relative to identical non-maleate-containing composites. NA means not available.

[b] CF is cellulose flour, EPP ethylene/propylene copolymer, MAPP maleated polypropylene, PP polypropylene, RGP refiner ground pulp, and WF wood flour.

[c] Compositions expressed as percentages by weight. MAPP-1 and MAPP-2 are low-molecular-weight maleated polypropylenes; MAPP-3 and MAPP-4 are high-molecular-weight maleated polyproylene. In reference (6), PP and MAPP reportedly contained elastomeric additives.

strength changes from −10 to +260 percent, tensile modulus from 0 to +90 percent, flexural strength and notched impact energy −10 percent, and unnotched impact energy from +50 to +100 percent.

The greatest improvements, at least in tensile properties, were achieved by Shiraishi's group using wood pulp fibers (about 0.2 mm long) with MAPP-3 polypropylenes grafted with 1 to 2 percent maleic anhydride.[4,6] In contrast, the other three groups referenced in Table I used wood pulp fibers or wood flour with small amounts of low molecular weight maleated polypropylene (MAPP-1 and MAPP-2) as additives; in these cases, the MAPP was used more truly as a coupling agent.[1,7,8]

What we designated as MAPP-1 in Table I is actually Eastman's Epolene E-43. This additive is available in large quantities but it is expensive compared with polypropylene and wood flour. We decided that Epolene E–43 warrants more detailed investigation as a property-enhancing additive in wood flour/polypropylene composities for high volume applications. We also felt that such an

investigation should be based on statistically designed test matrices to arrive at definitive conclusions regarding the effectiveness of the additive and the degree to which this effectiveness is altered by interactions with other primary system variables.

This paper reports the results of our first investigation, which was a full-factorial matrix study of four variables at two levels each. The four variables were Epolene E-43 content, wood flour particle size, wood flour to total polymer weight ratio, and number of extrusions. A subsequent paper will examine the effects of different Epolene-43 concentrations in combination with extrusion temperature.

## EXPERIMENTAL

### Test matrix

The matrix parameters and their values were as follows:

| Variable | Value |
|---|---|
| Epolene E-43 content | 0 or 5.0 percent by weight of dried (1 percent residual moisture) wood flour |
| Wood flour particle size | Nominal 20 or 40 mesh |
| Ratio of wood flour to total polymer | 45/55 or 55/45, dry weight basis |
| Extruder residence time | 1 or 3 passes |

The 5-percent Epolene E-43 level represents a compromise between cost and an attempt to achieve concentrations of anhydride moieties comparable to those reportedly producing significant improvement in mechanical properties.[1,4] The nominal 20- and 40-mesh wood flours are representative of those currently used in a commercial panel; however, the 20-mesh wood flour could conceivably offer advantages because of lower grinding costs, improved processibility, lower explosion hazard, and possibly a higher aspect ratio. The 45/55 and 55/45 wood flour to total polymer ratios cover the likely range for the commercial extruded panels, reflecting a compromise between the desirability for high loading (lower material costs) and decreased processibility at such a loading level. Multiple extruder passes obviously increase production cost, but we anticipated that extruder residence time might be an important factor for three reasons: (a) extrusion temperatures for wood-filled systems (about 200°C) approach the region of significant wood decompostion, which not only embrittles the wood particles but may also decrease their surface polarity and thus enhance their interaction with polypropylene and Epolene E-43; (b) dispersion of Epolene E-43 and wood flour in polypropylene improves with greater mechanical mixing; and (c) degree of reaction between wood and polymeric anhydride is a function of time at a given extrusion temperature.

The full-factorial matrix of 16 trials was performed in random order and subsequently replicated in a different random order. All other variables were held constant; for example, extruder barrel temperature was held at 200°C and injection molder barrel temperature at 215°C. The data were analyzed statistically using FACTDES,† Version 2.1.[9] Main effects, as well as two and three-way interactions, were determined for both 90 and 95 percent confidence limits based on an independent estimate of the experimental error from the complete replication (see Appendix for more detailed description of the analysis). Linear models were developed for the observed significant effects, and the residuals between the observations and model predictions were examined for any time biases (that is, nonrandom trends during the sequence of trials in a matrix).

## Materials

The polypropylene was Soltex Fortilene 9101 homopolymer spheres with a density of 0.900 g/mL and a melt flow index of 2.5 g/10 min (230°C/2160 g). Several stabilizers and processing aids were added to the polymer prior to processing: 0.10 percent Irganox-1010 (a tertiary butyl hydroxyhydrocinnamate) from McKesson Chemical, 0.20 percent Ionol (a butylated hydroxy toluene) from Ciba-Geigy Corporation, 0.10 percent GMS (mono- and diglycerides of fatty acids) from ICI United States, Inc., and 0.20 percent distearyl thiodipropionate (DSTP) from Witco Chemical. Epolene E-43 was obtained from Eastman Chemical Products, Inc.; the additive has a density of 0.934 g/mL, acid no. 47, and approximate molecular weight of 4,500. The wood flours were American Wood Fibers, Inc. no. 402 yellow pine, nominal 40-mesh, and no. 202 loblolly pine, nominal 20-mesh.



## Processing

The wood flour was vacuum dried at 50°C to 60°C for 24 h to a moisture content of 1 to 2 percent and then stored over desiccant in sealed containers. All other ingredients for a given trial were added to the dried wood flour and dry blended.

The 16 trials were extruded in random order with a Brabender 2503 Plasti-Corder 3/4 in., single-stage screw extruder (3-mm-diameter by 58-mm-long die) at 200°C barrel and die temperature, with a residence time of about 2 min. The extruded rod was pelletized and either stored dry immediately or re-extruded and repelletized two additional times. Test specimens were prepared in the same order using a Frohring Mini-Jector model SP50 (Newbury Industries, Inc.) plunger injection molding machine at 215°C with an average residence time of 1 to 2 min, ram pressure of 8.9 MPa, and mold temperature of about 25°C. After molding, the specimens were stored over desiccant at room temperature for at least 3 days before testing.

†The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

### Test methods

Each mechanical property was measured for 10 specimens from each trial. The desiccated specimens were measured at room temperature (about 23°C), with minimal exposure time to ambient humidity. Maximum tensile strength was measured in conformance with ASTM D 638M-84,[10] with specimen type IV at a nominal strain rate of 0.15 mm/mm-min. Specimens for flexural (three-point bending) and cantilever-beam tests were 127 by 12.7 by 3.2 mm. Three-point bending maximum strength and modulus were measured in conformance with ASTM D790-84a,[10] using a support span of 102 mm and a crosshead rate of 5 mm/min. Maximum flexural strength of cantilever-beam specimens was determined in conformance with ASTM D747[10] using a Tinius Olsen stiffness tester with a bending span of 50 mm and a rate of about 60°/min; a secant modulus was calculated from the load at 9°. Notched and unnotched impact energy was measured with an Izod impact tester; specimens were 64 by 12.7 by 6.4 mm, and tests conformed to ASTM D256-84.[10] Unnotched impact energy tests were performed on partial matrices only, and statistical analysis was not performed on those data. Densities were determined for specimens from the second matrix replicate only, using a neutral buoyancy method in a series of aqueous salt solutions. Relative melt viscosity was calculated as the ratio of Brabender pressure drop and throughput rate during the final extrusion of the three-pass trials of the second matrix replicate.

Wood flour particle size was determined by measuring the lengths and widths of two-dimensional optical projections of 250 to 300 particles per sample using microscopic views of an ethanol/glycerin dispersion of the powder. Particle areas were calculated by assuming the images to be quadrilateral.

Wood flour samples were obtained from the processed composites by xylene extraction of the gauge sections of tensile specimens from selected trials. Approximately 1-g samples were held in glass tubes containing coarse fritted glass discs and continuously eluted with hot xylene for 2 to 3 h while bathed in refluxing xylene. Prior to weighing, the initial sample and final residue were vacuum dried at about 70°C.



## RESULTS AND DISCUSSION

Table II summarizes the observed mechanical properties for all matrix conditions of the statistical design. Except for density, the values are the means and standard deviations of 20 measurements, 10 each from the two matrix replicates. The density values were determined using impact, bending, and tensile specimens from the second matrix replicate only.

Before we discuss the results in detail, three general observations are in order.

1. We conclude from the good reproducibility of the property measurements (Table II) that both the processing and testing methods were satisfactory. Coefficients of variation, for example, were approximately 0.7 percent for

TABLE II

Observed properties for study matrix conditions[a,b]

| Variable | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Wood flour/ polymer ratio[c] | Wood flour particle size (mesh) | Epolene E-43[d] (percent) | Extrusion (no.) | Flexural max. strength (MPa) | Cantilever beam max. strength (MPa) | Tensile max. strength (MPa) | Flexural modulus (GPa) | Cantilever beam secant modulus (GPa) | Notched impact energy (J/m) | Density (g/ml) |
| 45/55 | 20 | 0 | 1 | 44.7(1.3) | 52.9(1.4) | 27.3(0.6) | 4.00(0.18) | 3.96(0.20) | 52.7(4.2) | 1.055(0.004) |
| | | | 3 | 44.9(2.3) | 52.8(1.8) | 27.3(1.2) | 3.97(0.37) | 4.14(0.22) | 47.4(3.4) | 1.046(0.009) |
| | | 5 | 1 | 52.9(2.6) | 57.7(1.9) | 30.2(0.6) | 4.20(0.25) | 4.42(0.20) | 50.7(3.7) | 1.058(0.008) |
| | | | 3 | 50.6(2.6) | 57.4(1.7) | 31.2(0.9) | 4.17(0.26) | 4.70(0.15) | 45.3(2.6) | 1.067(0.010) |
| | 40 | 0 | 1 | 44.4(2.0) | 52.6(1.6) | 27.8(0.9) | 4.17(0.48) | 3.92(0.16) | 51.5(2.1) | 1.052(0.010) |
| | | | 3 | 44.7(1.5) | 52.0(1.7) | 28.8(0.5) | 4.67(0.33) | 4.27(0.30) | 46.3(4.0) | 1.055(0.006) |
| | | 5 | 1 | 55.7(3.1) | 60.4(1.8) | 33.0(1.1) | 5.05(0.36) | 4.85(0.18) | 44.9(4.2) | 1.056(0.007) |
| | | | 3 | 58.3(3.9) | 64.5(1.1) | 36.7(1.2) | 4.89(0.59) | 4.74(0.26) | 42.8(1.6) | 1.07 (0.007) |
| 55/45 | 20 | 0 | 1 | 43.9(2.1) | 50.7(1.8) | 24.4(0.6) | 4.52(0.27) | 3.92(0.14) | 55.6(4.0) | 1.091(0.006) |
| | | | 3 | 44.9(1.1) | 48.9(1.5) | 24.6(0.6) | 5.04(0.28) | 4.36(0.18) | 49.2(4.0) | 1.107(0.008) |
| | | 5 | 1 | 51.0(1.5) | 55.0(1.5) | 28.2(0.8) | 5.02(0.24) | 5.09(0.27) | 52.0(2.3) | 1.107(0.007) |
| | | | 3 | 52.3(2.9) | 55.5(1.1) | 28.3(1.2) | 4.78(0.38) | 4.87(0.23) | 44.0(2.9) | 1.113(0.004) |
| | 40 | 0 | 1 | 41.4(2.0) | 49.4(3.2) | 26.6(3.6) | 4.12(0.84) | 4.04(0.18) | 46.5(4.6) | 1.086(0.010) |
| | | | 3 | 43.6(1.5) | 47.0(1.2) | 25.0(0.7) | 5.28(0.38) | 4.18(1.17) | 45.4(2.6) | 1.112(0.005) |
| | | 5 | 1 | 53.5(3.5) | 55.4(1.8) | 29.5(1.6) | 5.33(0.39) | 5.01(0.28) | 45.4(2.8) | 1.105(0.008) |
| | | | 3 | 56.0(3.1) | 59.3(0.9) | 32.2(1.4) | 5.26(0.41) | 4.83(0.13) | 40.6(3.5) | 1.108(0.005) |

[a] Mean values. Values in parentheses are standard deviation.

[b] Density values are the mean of notched impact energy, cantilever-beam, and tensile specimens; 10 specimens from each matrix replicate. All other property values are the mean of 20 specimens, 10 for each matrix replication. The standard deviation reflects variations among specimens resulting from injection molding, property measurement, and matrix replication.

[c] Weight percentage of dry (1–2 percent moisture) wood flour.

[d] Dry weight basis. Polymer is polypropylene plus Epolene E-43.

density; < 5 percent for the three strength measurements and for the cantilever-beam modulus, all of which were derived from single-point force measurements; about 9 percent for the slope-derived flexural modulus; and about 7 percent for notched impact energy.

2. Analysis of the residuals between data and models showed no general time bias during each trial or between trials.

3. We note from Tables II and III and from the figures that the largest effects were caused by the addition of Epolene E-43; the greatest observed change, for example, was a 30 percent increase in flexural strength with 40-mesh wood flour in the 45/55 wood flour/polymer composition with the addition of 5 percent Epolene E-43 (Fig. 4). From a practical viewpoint, such an improvement may be highly useful.

## Effects of variables on mechanical properties

Table III shows the results of the statistical analysis, which include overall means and the magnitudes of main effects and second- and third-order interactions of



TABLE III

Main effects and interactions of variables on mechanical properties[a]

| Effect | Variable[b] | Strength properties (MPa)[c] | | | Flexural modulus[c] (GPa) | Cantilever beam secant[c] (GPa) | Notched impact energy[c] (J/m) | Density[d] (g/ml) |
|---|---|---|---|---|---|---|---|---|
| | | Flexural | Cantilever beam | Tensile | | | | |
| Overall mean | | 48.9 | 54.5 | 28.8 | 4.65 | 4.45 | 47.5 | 1.081 |
| Main effects[e] | WF/Pol | | −3.6 | −2.8 | 0.53 | 0.24 | | 0.046 |
| | Mesh | (+1.6) | 1.2 | 2.1 | 0.38 | 0.22 | −4.2 | |
| | E-43 | 9.7 | 7.4 | 4.6 | 0.37 | 0.64 | −3.6 | 0.01 |
| | Passes | | | | | 0:21 | −4.8 | 0.008 |
| Interactions[f] | WF/Pol × Mesh | | (−1.0) | | | (−0.15) | | |
| | WF/Pol × E-43 | | | | | −0.13 | | |
| | Mesh × E-43 | 2.7 | 2.3 | (+1.0) | | 0.26 | | |
| | Mesh × Passes | | | | | 0.15 | | |
| | E-43 × Passes | | 1.6 | | −0.33 | | | |
| | WF/Pol × MEsh × E-43 | | | | | | | |
| | WF/Pol × E-43 × Passes | | | | | | | (−0.008) |
| | Mesh × E-43 × Passes | | (+1.1) | | | | | |

[a] Values without parentheses are at 95 percent confidence limit; parenthetical values are at 90 percent confidence limit.

[b] WF is wood flour, Pol, total polymer; WF/Pol, wood flour/polymer ratio; mesh, wood flour particle size; E-43, Epolene E-43 content; and passes, number of extrusions.

[c] Mean of all 32 trials.

[d] Density data from single matrix. Effects derived using normal probability plot.

[e] Change in property resulting from the particular variable, averaged over all other variables.

[f] $X \times Y$ interaction = 1/2(average effect of $X$ at first level of $Y$ minus average effect of $X$ at second level of $Y$). $X \times Y \times Z$ interaction = 1/2 the difference between the $X \times Y$ interactions at the two levels of $Z$ (Ref. 19).

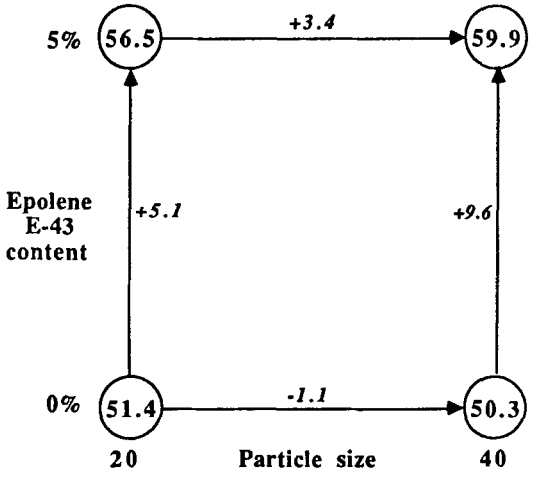


FIGURE 1 Two-factor interaction between Epolene E-43 content (0 or 5 percent) and wood flour particle size (20 or 40 mesh) for maximum cantilever-beam strength in megapascals. (Signficant at 95 percent confidence limit).



variables. Figures 1 to 3 are conventional statistical representations of two- and three-factor interactions. Figures 4 to 10 are three-dimensional plots of data from Table II for various strength properties, modulus, and notched impact energy. Figures 11 and 12 are two-dimensional plots for unnotched impact energy and density data. Note that Figures 4 to 12 should be regarded as "nonstatistical" in the sense that their dimensionality does not necessarily imply the existence of two- or three-factor interactions among the variables plotted. The primary purpose of these figures is to provide a picture of the effects and interaction of the variables, particularly the influence of Epolene E-43 content.

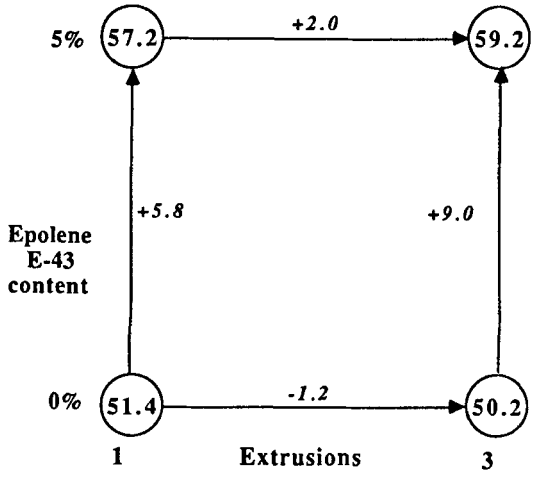


FIGURE 2 Two-factor interaction between Epolene E-43 content (0 or 5 percent) and number of extrusions (1 or 3) for maximum cantilever-beam strength in megapascals. (Significant at 90 percent confidence limit).

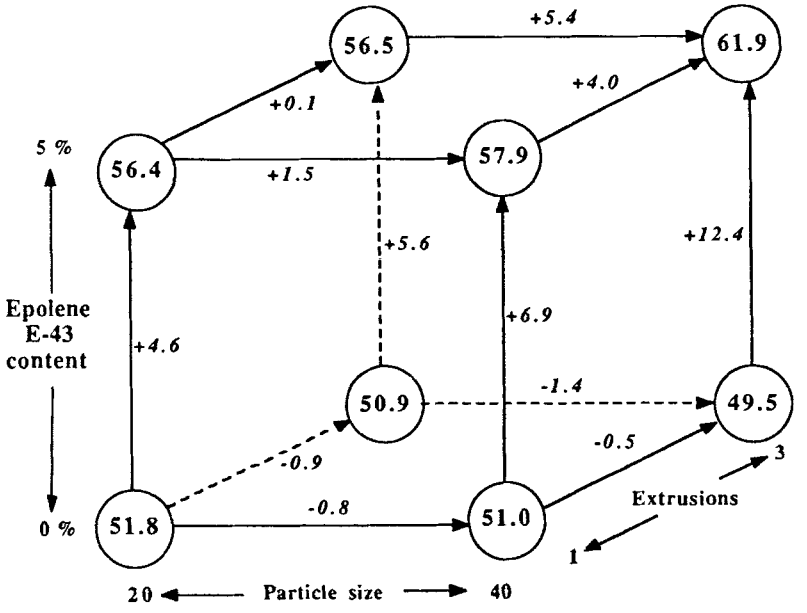


FIGURE 3 Three-factor interaction of Epolene E-43 content (0 or 5 percent), wood flour particle size (20 or 40 mesh), and number of extrusions (1 or 3) for maximum cantilever-beam strength in megapascals. (Significant at 90 percent confidence limit).

## Strength

A strong, though not complete, correlation occurred among the main effects and interactions of the variables for flexural, cantilever-beam, and tensile strength (Table III, Figures 1 to 7). In fact, these strength properties were themselves highly correlated; the correlation coefficient between cantilever-beam and three-point-bending strengths was 0.86 and that between cantilever-beam and tensile strengths 0.90. Epolene E-43 had the strongest effect on strength, followed by the wood flour/polymer ratio and wood flour particle size. The strongest interaction occurred between particle size and Epolene E-43 content. Figure 1 illustrates the effect of this interaction on cantilever-beam strength; smaller particle size decreased the strength in the absence of Epolene E-43 but increased strength when the additive was used. Figure 2 shows a somewhat smaller interaction between Epolene E-43 and number of extrusions; multiple extrusions decreased strength in the absence of Epolene E-43 but increased strength when the additive was used. Finally, Figure 3 illustrates a three-factor interaction of Epolene E-43, particle size, and number of extrusions; the optimum condition was addition of Epolene E-43, 40-mesh wood flour, and three extrusions.

The response surfaces in Figures 4 to 7 clearly show the increases in maximum strengths that resulted from the addition of Epolene E-43. The response surfaces for the 5-percent Epolene E-43 system are all consistently above those for 0-percent additive. On the other hand, the smaller wood flour particle size was advantageous only in the presence of Epolene E-43. The number of extrusions exerted only a small effect on strength; this effect was significant only when

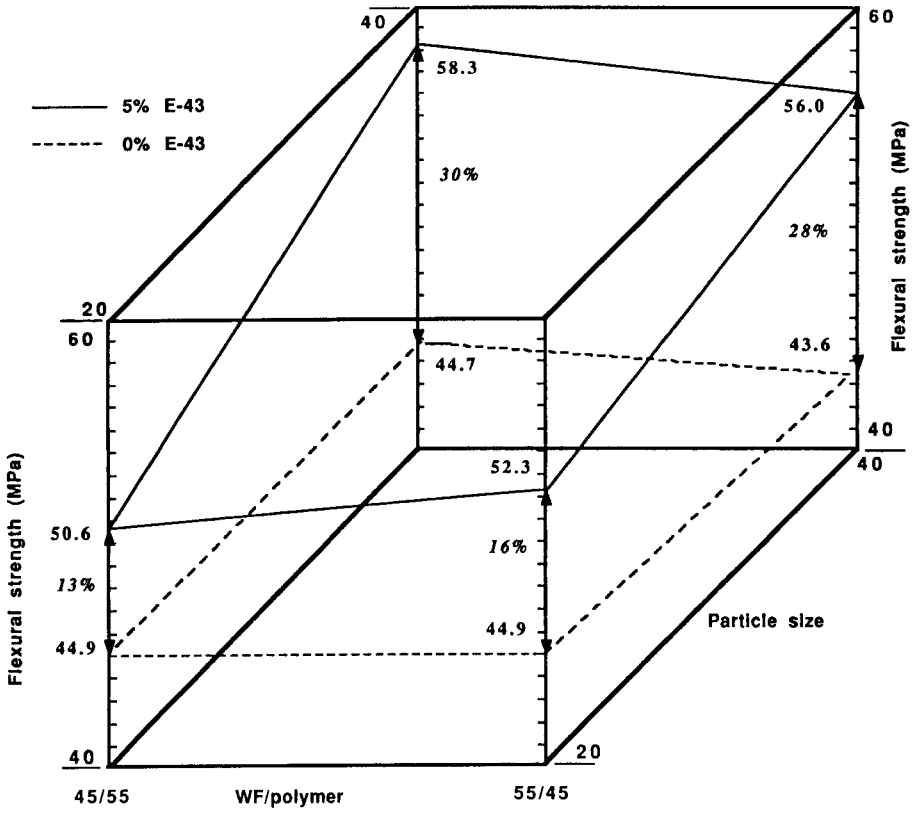


FIGURE 4 Maximum flexural strength as a function of wood flour to total polymer weight ratio (WF/polymer), wood flour particle size, and Epolene E-43 content. (All data points are the average of results for one and three extrusions. Epolene E-43 levels are weight percentages of wood flour.)

Epolene E-43 was present (Figures 3, 7), and the effect was possibly enhanced with smaller wood particles. Therefore, the greatest overall increases in strengths resulting from the addition of Epolene E-43 approached 30 percent. These improvements were seen with the finer wood flour, and, to a lesser extent, after three extrusions.

The predominant influence of Epolene E-43 in increasing composite strength (and modulus; Figures 8, 9) indicates that some coupling action occurs, leading to greater reinforcement by the wood particles. Further evidence is given by the positive interaction between increases in surface area and Epolene E-43 content (Table III) and the positive effect of greater particle surface area (Table IV).

Similarly, the small positive interaction between Epolene E-43 content and number of extrusions is consistent with better dispersion of the additive and wood particles and/or greater reaction between the wood and the anhydride groups of Epolene E-43. In this connection, it is noteworthy that the surface area per particle was decreased by processing, particularly in the presence of Epolene E-43 (Table IV). In view of the minor changes in melt viscosity that occurred with the

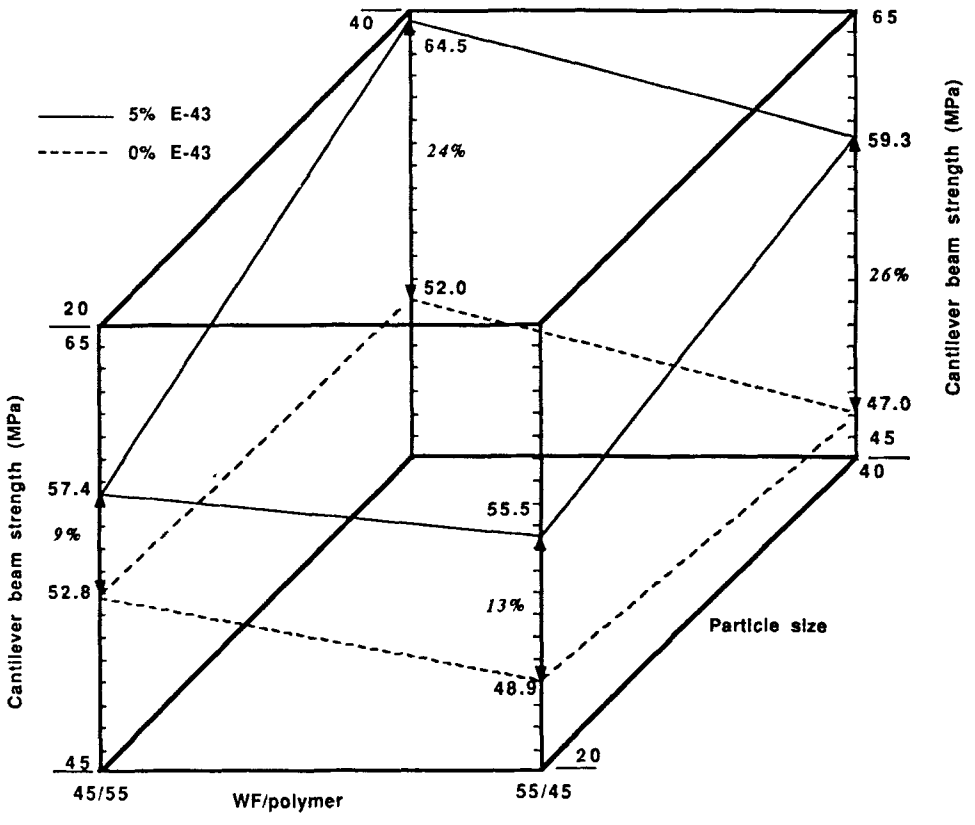


FIGURE 5 Maximum cantilever-beam strength as a function of wood flour to total polymer weight ratio, wood flour particle size, and Epolene E-43 content. (All data points are the average of results for one and three extrusions. Epolene E-43 levels are weight percentages of wood flour.)

addition of Epolene E-43 (Table V), the greater surface area reduction in the presence of the additive was apparently not caused by larger shear stresses. Instead, we suggest that the acidic nature of the additive accelerated the degradation of cellulose at the melt processing temperatures, leading to embrittlement of the wood particles. This explanation is consistent with the observed darker color of the composite containing Epolene E-43.

The strength increases observed in our study attributable to Epolene E-43 confirm findings from other studies with low-molecular-weight MAPP (Table I, Refs. 1, 7, 8). The greater strength improvement shown by Hyche and Barbarito[7] with about half as much Epolene E-43 as we employed may indicate that we exceeded the optimum concentration.

The strength losses observed on increasing the wood flour content from 45 to 55 percent (see Figures 4, 5) are consistent with expectations for a weakly reinforcing filler. For nonadhering spheres in a polymer matrix, the influence of filler volume fraction $v_f$ on composite strength is reportedly proportional to $(1 - v_f)$ (Ref. 11) or to $(1.00–1.21\ v_f^{2/3})$ (Ref. 12). In the first case, the ratio of

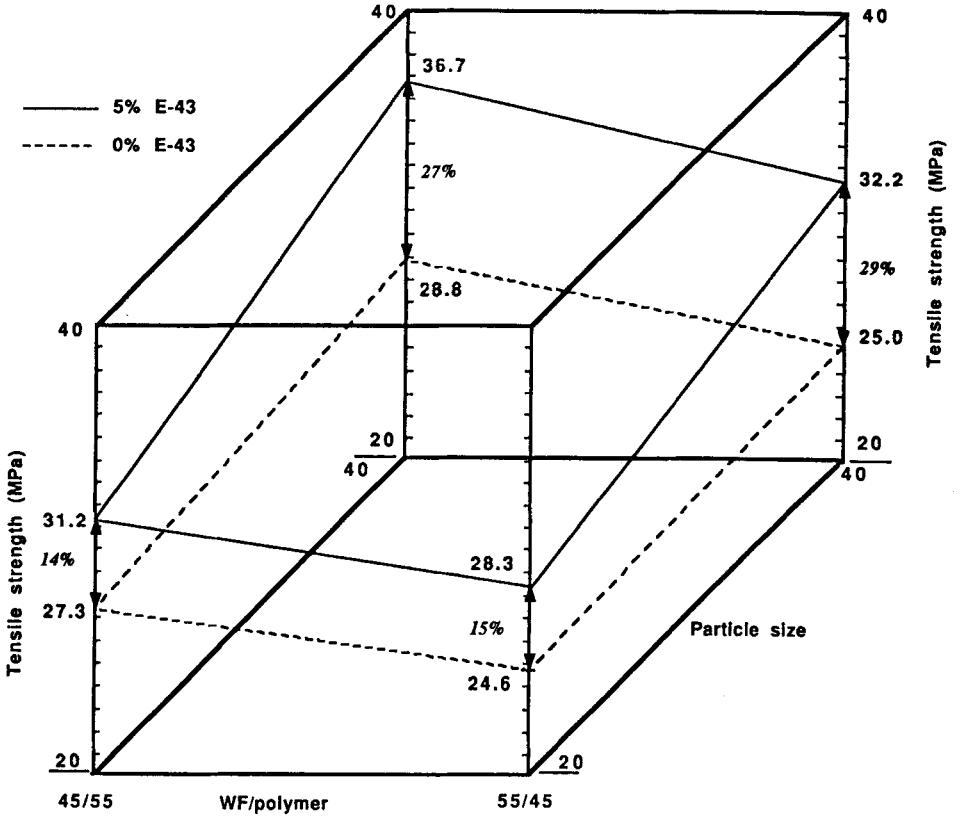


FIGURE 6 Maximum tensile strength as a function of wood flour to total polymer weight ratio, wood flour particle size, and Epolene E-43 content. (All data points are the average of results for one and three extrusions. Epolene E-43 levels are weight percentages of wood flour.)



strengths for 55/45 to 45/55 wood flour/polymer composites should be 0.84, and for the second case 0.75. The observed strength ratios (after pooling over the other variables) were 0.90, 0.94, and 0.98 for tensile, cantilever-beam, and flexural strength, respectively. The higher observed values may be attributable to the presence of some particle-polymer adhesion and/or to particle aspect ratios somewhat above 1.

The small increase in strength with smaller wood flour particle size (20 mesh compared to 40 mesh, Table IV) is qualitatively consistent with experimental and theoretical studies on spherical particles that show an inverse dependence of strength on the square root of diameter.[11,13–15] Quantitative comparisons with theory would not be realistic. Given good particle dispersion and some degree of particle-matrix bonding, we can expect the larger particle system to possess greater stress concentrations and poorer particle-matrix stress transfer.

## Modulus

The flexural modulus was significantly increased by increasing the wood flour to polymer ratio, decreasing particle size, and adding Epolene E-43 (Table III,

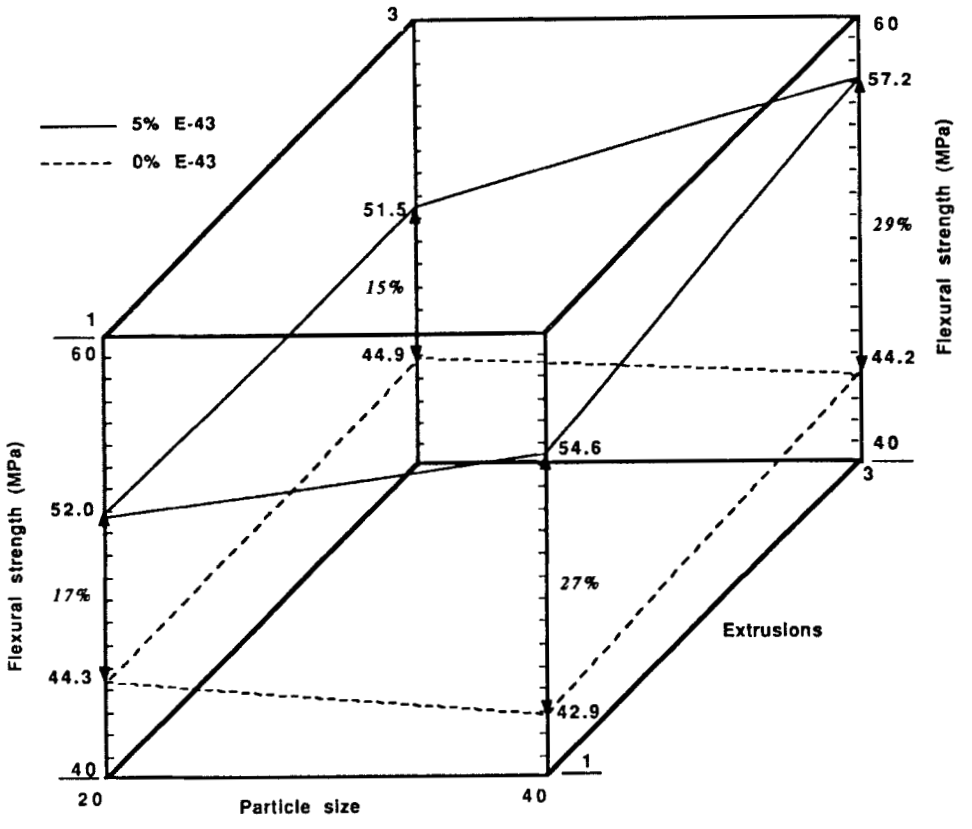


FIGURE 7 Maximum flexural strength as a function of wood flour particle size, number of extrusions, and Epolene E-43 content. (All data points are the average of results for 45/55 and 55/45 weight ratios of wood flour to total polymer.)

Figure 8); the wood flour to polymer ratio had the greatest effect. The number of extrusions was effective only as a negative interaction with Epolene E-43. In contrast, the cantilever-beam modulus was significantly affected in a positive direction by all four factors and exhibited several two-way interactions (Table III, Figure 9); Epolene E-43 exerted the greatest effect on this property. In the response surfaces in Figures 8 and 9, the lowest values are clearly found with the combination of lower wood flour content, larger particle size, and absence of Epolene E-43. Conversely, the highest values are found with the combination of higher wood flour content, smaller particle size, and presence of Epolene E-43. The greatest effect of Epolene E-43 was a 27 percent increase in cantilever-beam modulus with the 55/45 wood flour/polymer ratio and 40-mesh flour (Figure 9).

As with the strength properties, the positive effect of Epolene E-43 on modulus indicates some coupling action. This is supported by the positive effect of the smaller wood flour particle size. The expected effect of wood flour content on modulus can be approximated by the Tsai-Halpin equation.[1] Assuming moderately close-packed spheres, the result for the modulus ratio of our 55/45 to 45/55

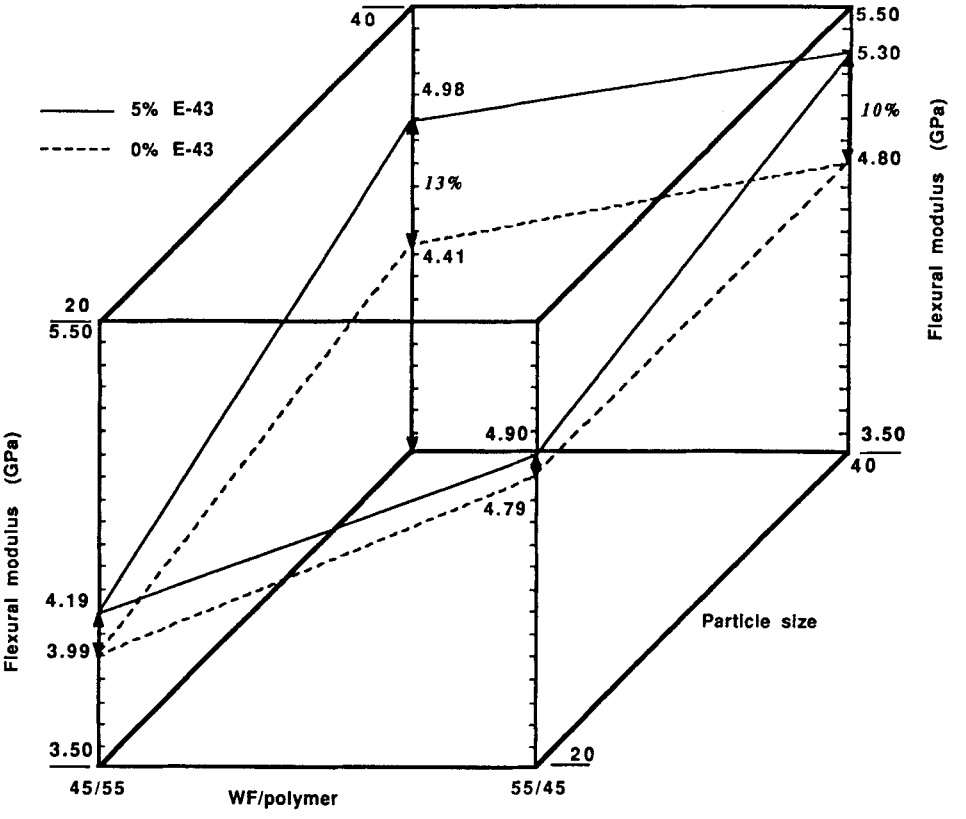


FIGURE 8 Flexural modulus as a function of wood flour to total polymer weight ratio, wood flour particle size, and Epolene E-43 content. (All data points are the average of results for one and three extrusions. Epolene E-43 levels are weight percentages of wood flour.)



systems is about 1.02. The experimental values for that ratio, averaged over the other three factors, were 1.11 for flexural modulus and 1.05 for cantilever-beam modulus. The higher experimental ratios are consistent with aspect ratios that are slightly above 1 and/or with some degree of coupling.

## Impact energy

The smaller particle size, larger number of extrusions, and addition of Epolene E-43 decreased notched impact energy $\leq 10$ percent (Table III, Figure 10). On the other hand, a nonstatistical analysis of the unnotched impact energy data (Figure 11) indicated that this property was decreased by the higher wood flour content and increased by smaller particle size at the lower wood flour content. On average, unnotched impact energy was unaffected by Epolene E-43, but it did appear to be enhanced by the additive at the lower wood flour content. The existence of different trends for the two measurements of impact energy is not surprising. Unnotched impact behavior is controlled to a considerable extent by

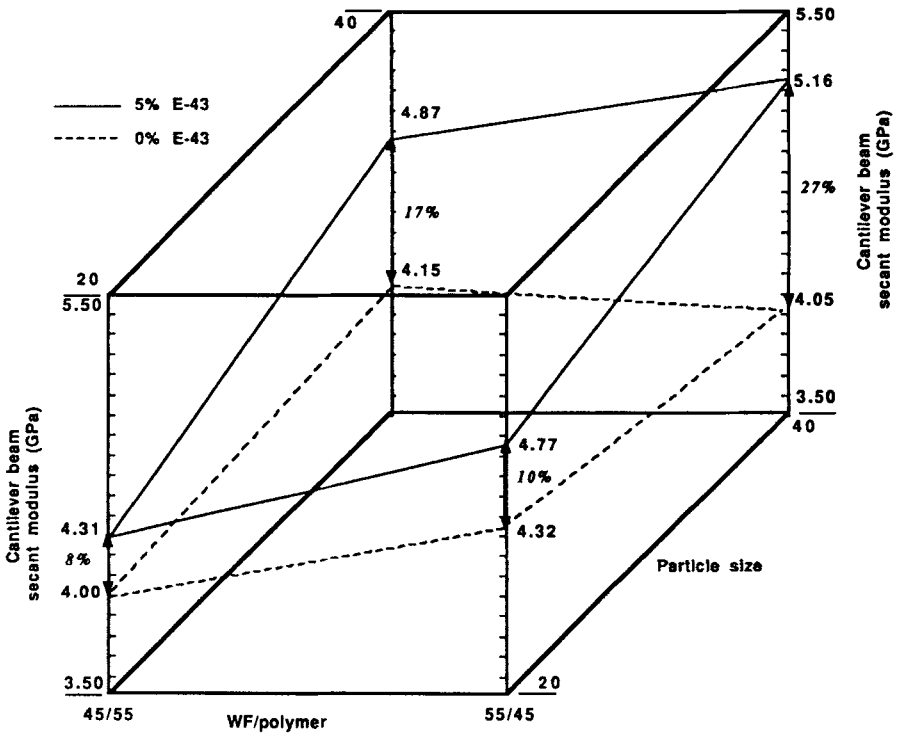


FIGURE 9 Cantilever beam secant (9°) modulus as a function of wood flour to total polymer weight ratio, wood flour particle size, and Epolene E-43 content. (All data points are the average of results for one and three extrusions. Epolene E-43 levels are weight percentages of wood flour.)



fracture initiation processes, which, in turn, are controlled by stress concentrations at defects in the system. By contrast, notched impact behavior is controlled to a greater extent by factors affecting the propagation of fracture initiated at the predominating stress concentration at the notch tip.[16]

For calcium-carbonate-filled polypropylene composites, unnotched impact energy has been shown to fall with increasing fractions of large particles or

TABLE IV

Wood flour particle area[a]

| Variable | Particle area ($mm^2$) | | | |
|---|---|---|---|---|
| | 20 mesh | | 40 mesh | |
| | Mean | Maximum | Mean | Maximum |
| Unprocessed flour | 0.18 | 1.1 | 0.080 | 0.30 |
| Processed flour[b] | | | | |
| 0 percent Epolene E-43 | 0.095 | 0.65 | 0.026 | 0.20 |
| 5 percent Epolene E-43 | 0.039 | 0.35 | 0.010 | 0.12 |

[a] Measured from two-dimensional projection of specimens after xylene extraction.

[b] Three extrusions at 45/55 weight ratio of wood flour to polymer.

TABLE V

Relative melt viscosity of composites[a]

| Variable | Melt viscosity[b] (kPa per g/s) |
|---|---|
| Wood flour to polymer ratio | |
| 45/55 | 2.30 |
| 55/45 | 2.43 |
| Wood flour particle size | |
| 20 mesh | 2.40 |
| 40 mesh | 2.34 |
| Epolene E-43 content | |
| 0 percent | 2.30 |
| 5 percent | 2.44 |

[a] Extruder pressure drop divided by throughput rate.

[c] Pooled mean (mean over all other variables).



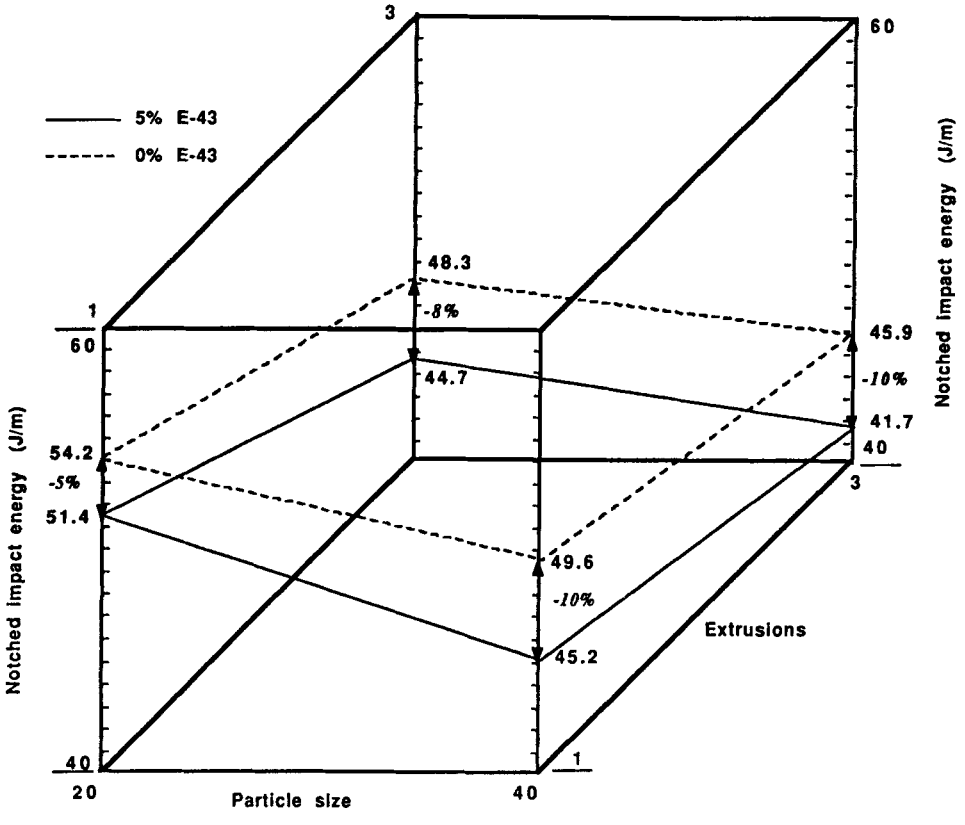


FIGURE 10 Notched impact energy as a function of wood flour particle size, number of extrusions, and Epolene E-43 content. (All data points are the average of results for one and three extrusions. Epolene E-43 levels are weight percentages of wood flour.)

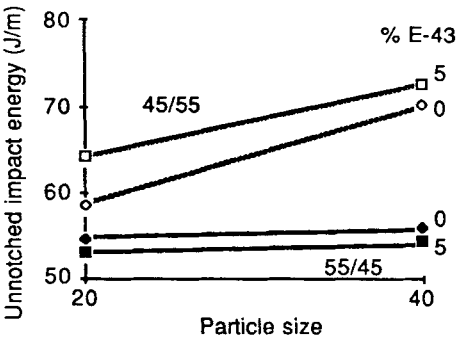


FIGURE 11 Unnotched impact energy as a function of wood flour particle size (20 or 40 mesh), wood flour to total polymer weight ratio (45/55 or 55/45), and Epolene E-43 content (partial test matrices).

agglomerates,[17] presumably as a consequence of the attendant stress concentration regions. Thus, our observed decrease in unnotched impact energy with the higher wood flour to polymer ratio (Figure 11) may be attributable to a greater concentration of large particles or even agglomerates (defects). Similarly, our observed increase in unnotched impact energy with smaller particle size at the lower wood flour content can be rationalized on the basis of smaller defects. The apparent increase in unnotched impact energy with Epolene E-43 and the 45/55 wood flour/polymer ratio is smaller than, but in the same direction as, that seen by Dalvag and coworkers[1] for their 29/71 wood flour or fiber/polymer system (Table I); the increase in unnotched impact energy shown in our study may also be the consequence of better particle dispersion in the matrix and smaller particle size (Table IV).

Interpretations are less obvious for the decrease in notched impact energy with smaller particle size, addition of Epolene E-43, and greater number of extrusions. However, we have noted that the improved strengths that accompanied smaller particle size and addition of Epolene E-43 were consistent with a greater interaction between filler and matrix. Such an interaction could also inhibit polymer mobility and thereby lower the ability of the system to absorb energy during fracture propagation. In addition, increasing the number of extrusions may enhance the filler-polymer interaction, but it may also embrittle the wood through degradation. The observed decrease in notched impact energy with addition of Epolene E-43 is comparable to that reported by Hyche and Barbarito (Table I).

## Density

Increasing the wood flour to polymer ratio significantly increased density, as expected (Table III, Figure 12). Assuming that the wood flour pores are either completely filled with polymer or are collapsed by the molding pressure, the effective density of the wood flour should be about 1.45 g/ml. This, combined with a polypropylene density of 0.90, leads to a calculated density increase of 0.047 g/ml between the 45/55 and 55/45 wood flour/polymer ratios. The observed

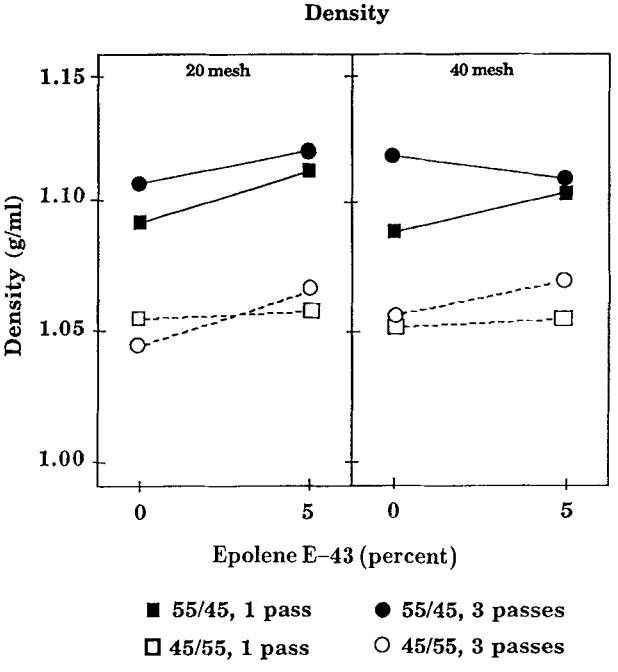


FIGURE 12 Effect of wood particle size, Epolene E-43 content, wood flour to polymer ratio, and number of extrusions on density.



magnitude of the change was 0.046 g/ml, indicating the assumption of particle penetration or collapse is valid. The small increase of 0.01 g/mL observed upon adding Epolene E-43 is still 10 times that calculated from the greater density of the additive relative to polypropylene. We presume, therefore, that the observed increase in density resulted from either enhanced dispersion and wetting or from nucleation of polymer crystallization. We offer a similar explanation for the slight density increase that accompanied an increase in the number of extrusions.

## Melt viscosity

We examined the effects of the four variables on melt viscosity in much less detail, and we include the results only as preliminary indications of those effects. As judged by the ratios of Brabender pressure drop to throughput rate (Table V), the relative melt viscosity of the various composites underwent little change. On average, for example, the changes were as follow:

| Variable | Change in melt viscosity (percent) |
|---|---|
| 45/55 to 55/45 wood flour/polymer ratio | +6 |
| 20- to 40-mesh wood flour | −3 |
| 0 to 5 percent Epolene E-43 content | +6 |

Although the incomplete matrix here precludes a statistical analysis, these

changes are probably not significant. In contrast to the small or nonexistent effect we observed on adding Epolene E-43, Dalvag and coworkers reported that MAPP-2 caused a substantial increase in melt viscosity with both wood flour and cellulose fibers.[1] One can imagine that the additive could have two extreme effects on the melt viscosity of filled thermoplastics.[18] If the additive were coupling the filler and polymer by chemical bonds, flow resistance and viscosity should increase. On the other hand, if the additive were simply coating the particles and acting as a wetting or lubricating agent, flow resistance and viscosity should decrease. Within the melt, Epolene E-43 may be chemically bonded to the particles but may interact only weakly with the matrix polymer; thus, the net effect of the additive on flow resistance could be relatively weak. In addition, its low molecular weight will cause some lowering of matrix viscosity if a significant fraction is not adsorbed by the filler.

## Economic considerations

From the viewpoint of the current major application—e.g., for the interior panel of a car—we expect that the optimum product should be one with high flexural strength and modulus and high unnotched impact energy. As Table VI indicates, the best combination of those properties is probably achieved with the 45/55 wood flour/polymer ratio in the presence of Epolene E-43. Unfortunately, that is also the most expensive system in terms of cost of materials (34¢/lb). However, in the 55/45 wood flour system with Epolene E-43, the high cost of the additive is more than compensated by the low cost of the wood flour and medium cost of polypropylene, resulting in a materials' cost of 30¢/lb. The 55/45 wood flour system provides strength and modulus properties close to those of the 45/55 system with Epolene E-43, at a sacrifice of a somewhat reduced impact resistance.



TABLE VI

Effect of wood flour/polymer ratio and Epolene E-43 content of composites on selected mechanical properties and cost of materials[a]

| Product composition[b] | Cost of materials[c] (¢/lb) | Flexural strength[d] (MPa) | Flexural modulus[d] (GPa) | Unnotched impact energy[d] (J/m) |
|---|---|---|---|---|
| 45/55 WF/polymer ratio | | | | |
| 0 percent Epolene E-43 | 0.31 | 45 | 4.4 | 70 |
| 5 percent Epolene E-43 | 0.34 | 58 | 5.0 | 73 |
| 55/45 WF/polymer ratio | | | | |
| 0 percent Epolene E-43 | 0.26 | 44 | 4.8 | 55 |
| 5 percent Epolene E-43 | 0.30 | 56 | 5.3 | 54 |

[a] Values are approximate.
[b] Wood flour/polymer (WF/polymer) ratio calculated per dry weight of wood flour.
[c] Assumed cost of wood flour 7¢/lb, polypropylene 50¢/lb, and Epolene E-43 $1.60/lb.
[d] Mean of 1 and 3 extrusions and 40-mesh wood flour particles.

## SUMMARY AND CONCLUSIONS

A four-factor, two-level, full-factorial statistical design was followed to establish the influence of four composition or processing variables on several mechanical properties of a wood flour/polypropylene composite. The four variables and their levels were wood flour to total polymer weight ratio (45/55 or 55/45), wood flour particle size (20 or 40 mesh), presence or absence of a maleated polypropylene (Epolene E-43), and number of extrusions (one or three). Major findings and conclusions are as follows:

1. Of the four variables, the Epolene E-43 additive most strongly influenced the flexural, cantilever-beam, and tensile strength of the composite. The influence was most pronounced with the smaller particle-size flour, and, to a lesser extent, after three extrusions. Epolene E-43 exerted the greatest effect on flexural strength (30 percent increase) in combination with 20-mesh flour at the 45/55 wood flour/polymer ratio. (Averaged over all other variables, the observed strength increases caused by Epolene E-43 amounted to 13 to 20 percent.) These responses indicate some degree of coupling action by Epolene E-43 and represent significant improvements from a practical viewpoint.

2. The largest values of flexural and cantilever-beam modulus were seen with the combination of the 55/45 wood flour polymer ratio, 20-mesh flour, and addition of Epolene E-43. For example, for this combination, addition of the additive increased the cantilever-beam modulus by 27 percent.

3. Although the incomplete unnotched impact energy data could not be statistically analyzed, the notched and unnotched impact energies apparently responded differently to the study variables. The greatest effect was a nearly 30 percent increase in unnotched impact energy with the 45/55 wood flour/polymer ratio and 40-mesh flour. All other combinations resulted in $\leq 10$ percent change in impact energy.

4. Based on the ratio of extruder pressure drop to throughput rate, the range of variables had little influence on melt viscosity.

5. The largest effect on composite density resulted from increasing the wood flour to polymer ratio from 45/55 to 55/45. The observed 5-percent increase can be quantitatively rationalized, assuming the wood flour pores are fully penetrated or collapsed.

6. Within the range of variables examined, the best balance of properties can be obtained with the system that has the highest materials' cost—45/55 wood flour/polymer ratio and 5-percent Epolene E-43. That cost penalty can be alleviated by changing the wood flour to polymer ratio to 55/45. The latter system possesses nearly the same strength and stiffness as the former but results in lower impact resistance.

A complete evaluation of the utility of Epolene E-43 in relationship to cost will require data from tests using other Epolene E-43 concentrations. In addition, we can expect that different extrusion temperatures will alter the effectiveness of the

additive because temperature affects wood degradation and the reaction between wood and anhydride groups. Moreover, the positive effects of Epolene E-43 on mechanical properties of wood flour composites suggest greater improvements in composites containing wood fibers, which have higher aspect ratios.

## ACKNOWLEDGEMENTS

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## APPENDIX I–STATISTICAL ANALYSIS

Where data from a complete matrix were available for a particular response, they were statistically analyzed using FACTDES, Version 2.1.[9] For density values that were available for only one matrix replicate, the analysis was based on a comparison with standard probability distributions. For those responses with data from both complete replicates, the analyses were based on an independent estimate of the experimental error from the complete replication. For example, using the maximum cantilever-beam strength as a response, the two response sets are shown in Table A-1 in standard order. Also shown are the differences in

TABLE A-1

Multifactorial design with replicated responses

| Standard trial order | Independent variable | | | | Cantilever-beam strength (MPa) | | Difference in response ($d_i$) |
|---|---|---|---|---|---|---|---|
| | Wood flour (percent) | Particle size (mesh) | Epolene content (percent) | Extrusion (number) | First replicate | Second replicate | |
| 1 | 45 | 20 | 0 | 1 | 53.1 | 52.6 | 0.5 |
| 2 | 55 | 20 | 0 | 1 | 51.8 | 49.5 | 2.3 |
| 3 | 45 | 40 | 0 | 1 | 51.8 | 53.3 | 1.5 |
| 4 | 55 | 40 | 0 | 1 | 52.0 | 46.8 | 5.2 |
| 5 | 45 | 20 | 5 | 1 | 56.1 | 59.2 | 3.1 |
| 6 | 55 | 20 | 5 | 1 | 54.0 | 56.0 | 2.0 |
| 7 | 45 | 40 | 5 | 1 | 60.1 | 60.7 | 0.6 |
| 8 | 55 | 40 | 5 | 1 | 56.7 | 54.1 | 2.6 |
| 9 | 45 | 20 | 0 | 3 | 51.7 | 53.9 | 2.2 |
| 10 | 55 | 20 | 0 | 3 | 48.2 | 49.6 | 1.4 |
| 11 | 45 | 40 | 0 | 3 | 51.4 | 52.6 | 1.2 |
| 12 | 55 | 40 | 0 | 3 | 46.2 | 47.7 | 1.5 |
| 13 | 45 | 20 | 5 | 3 | 56.2 | 58.6 | 2.4 |
| 14 | 55 | 20 | 5 | 3 | 54.7 | 56.3 | 1.6 |
| 15 | 45 | 40 | 5 | 3 | 64.0 | 64.9 | 0.9 |
| 16 | 55 | 40 | 5 | 3 | 59.0 | 59.5 | 0.5 |



response ($d_i$) at each of the 16 unique trials. These differences provide an independent estimate of the experimental error because both sets of trials were run in a different random order at a different time. In the case of cantilever-beam strength, the estimate of the standard deviation of each effect is 0.543, and the appropriate t-value for 16° of freedom and a 90 percent confidence interval is 1.746.

The standard deviation of an effect is found from

$$S^2_{\text{pooled}} = \frac{\sum d_i^2/4}{16} = 1.18$$

and

$$\text{Standard deviation (effect)} = \sqrt{\frac{S^2_{\text{pooled}}}{4}} = 0.543$$

The corresponding 90 percent confidence interval is expressed as Effect $\pm$ $(1.746 \times 0.543)$. If the confidence interval includes zero, then the effect is not statistically significant at a risk of 10 percent.

Thus, for the maximum cantilever-beam strength response, the following effects are statistically significant at the 90 percent confidence level.

| Independent variable | Magnitude of effect |
|---|---|
| Wood flour/polymer ratio | −3.63 |
| Wood flour particle size | 1.21 |
| Epolene E-43 content | 7.37 |
| Particle size/Epolene E-43 interaction | 2.28 |
| Epolene E-43/number of extrusions interaction | 1.62 |

For instance, adding Epolene E-43 increased the cantilever-beam strength by 7.37 MPa on the average over all combinations of the four factors. Changing the ratio of wood flour to polymer from 45/55 to 55/45 decreased the strength by 3.63 MPa on the average. Also significant in this case were the two-way interactions between Epolene E-43 and particle size, and Epolene E-43 and number of extrusions.