

Mechanical Properties and Crack Propagation of Soy-Polypropylene Composites

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ABSTRACT: Composites from soy flour (SF) and polypropylene (PP) exhibited increased impact and flexural properties when SF was treated with potassium permanganate (KMnO₄) or when subjected to autoclave treatment and maleic anhydride coupling agent addition. The impact strength increased by at least 13% for the KMnO₄ SF composites and by 18% for the autoclave SF composites with maleic anhydride coupling agent addition. These two SF composite materials showed increased impact and flexural modulus, an indication of multiscale material architecture. Scanning electron microscopy imaging of the fractured surfaces revealed different morphology and potential crack propagation mechanisms. Composites with untreated SF showed poor bonding with the polypropylene matrix whereas improved bonding was observed for SF subjected to KMnO₄ treatment. Composites with SF subjected to autoclave treatment combined with maleic anhydride revealed good bonding. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 175–185, 2013

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INTRODUCTION

Composites in automotive applications are used in the exterior and interior parts. The main advantage of agricultural fillers for the preparation of composites is their light weight due to their low density in comparison to mineral fillers (calcium carbonate, talc) or inorganic fibers (glass fiber). Studies have investigated composites with polyolefins containing a range of agricultural fillers.^{1–5} Most fillers investigated are high cellulose materials and were selected for their structural features. Soy meal represents a different category of filler which has negligible structural features and contains proteins (40–50%) and carbohydrates (30%) as major constituents.

When developing composites from agricultural fillers and polyolefins, their incompatibility due to differences in surface properties remains a major challenge. Fillers derived from agricultural resources are hydrophilic. Polyolefins on the other hand are hydrophobic. Therefore the two materials are difficult to mix and have minimal interaction resulting in poor mechanical properties.^{6–8} Surface modification and the addition of coupling agents are known to improve the interaction between the surface of the dispersed and the continuous material by creating chemical bonds.^{6,9–11} Surface modifications that alter the properties of the materials can be chemical or physical and can target the filler or the polymer matrix.^{9,10,12–15} Combinations of treatments are also possible.^{6,16,17} Most developments have

focused on composites with high cellulose and/or lignin agricultural materials and have shown to be inefficient when applied to soy flour.¹⁸ Thus alternative methods should be developed that consider the protein content, in addition to the cellulose content, of agricultural materials and improve their thermal stability and the impact properties of the composites. When improving the toughness of a material, often the flexibility is sacrificed because both properties generally will behave as “mutually exclusive”.¹⁹ However, a few materials exist where both properties are mutually inclusive. The most advanced examples of such materials are natural materials that contain highly ordered multi-scale structures, from nano, to micro and macro scale.¹⁹

Chemical and thermal treatments of agricultural and plant materials have been considered for the development of high performance materials or bio-refineries²⁰ and for the improvement of the nutritional characteristics of food products. Oxidation by potassium permanganate is a well-established treatment in the paper industry that increases carbonyl and carboxyl groups.²¹ Heat treatment has been extensively studied for the improvement of the nutritional value of soy products, e.g. soy flours, grits, and proteins.²² Potassium permanganate is also known to oxidize the surfaces of polymers such as PP, PE, and PET.^{23,24}

In this study, the contribution of coupling agents, soy flour treatment methods and soy flour constituents was investigated

Table I. Mass Ratio of Water, Soy Material, and KMnO_4 for Potassium Permanganate Treatment

Soy material	Parts water	Parts soy material	Parts KMnO_4
SF	6	2	1
IS	12	2	1
SPI	20	2	1
SH	6	2	1

for their effect on the mechanical properties of soy-polypropylene composites. Correlations between impact strength and flexural modulus were identified. Scanning electron microscopy (SEM) imaging revealed differences of the interaction between soy materials and polypropylene. Proposed crack propagation mechanisms were developed based on the SEM imaging.

EXPERIMENTAL

Materials

Defatted soy meal and soy hulls (SH) were obtained from Bunge (Hamilton, Canada). Soy protein isolate (SPI (c)) Pro-Fam 974 was obtained from Archer Daniels Midland (ADM) Company (Decatur, USA) and used as received since its particle size was less than 0.08 mm. Polypropylene, a blend of homo- and copolymer, was provided by A. Schulman (USA). The melt flow index of the polypropylene blend measured at 230°C and 2.16 kg load was 27 g/10 min.²⁵

Preparation of Soy Materials

Soy Flour Preparation and Processing. Soy flour (SF) was obtained by milling soy meal, with an ultracentrifugal mill ZM200 (Retsch GmbH, Germany) and 0.08 mm sieve with trapezoid-shaped holes (part # 03.647.0231).

Soy flour was processed to produce a number of fractions as illustrated in Figure 1. Namely, an aqueous soy flour mixture was prepared with ultrapure water and pH adjustment to 9.0 with 1M NaOH. The mixture was heated to 50°C under stirring on a magnetic stirrer for one hour. The mixture was centrifuged at 10,000 rpm ($\text{RCF}_{\text{max}} = 11,200$) for 20 min (Sorvall WX 100 with A-621 rotor, Thermo Scientific, USA) and the solid residue [insoluble fraction (IS)] was dried at room temperature in a fume hood (relative humidity (RH) < 20%). The supernatant, containing mostly proteins, sugars, and minerals, was adjusted with 1M H_2SO_4 (95–98%, GR ACS, Fisher Scientific, Canada) to pH 4, just below the isoelectric point of the major soy proteins (glycinin and conglycinin) and centrifuged at 10,000 rpm. The resulting precipitate is referred as soy protein isolate [SPI (ex)]. The remaining liquid solution, containing mostly sugars and minerals, represented the soluble sugar extract (SSE).

Prior to their use or treatment, IS and SPI (ex) were milled as described previously. After treatment, the soy materials were dried in a fume hood (RH < 20%) at room temperature (RT) until their moisture content was below 5%.

Autoclave Treatment. The soy material (~ 500 g), placed on a glass tray and having height less than one centimeter, was placed in a direct steam heated sterilizer-autoclave for steriliza-

tion of biological materials (Consolidated Still & Sterilizers, USA) and subjected to 125°C and steam for 25 min. The treated soy material was then dried and milled as described previously for soy meal.

Potassium Permanganate (KMnO_4) Chemical Treatment. An aqueous soy material solution containing potassium permanganate (KMnO_4 , GR ACS, EMD, USA) was prepared at room temperature with a KMnO_4 to soy material 1:2 mass ratio. The volume of water added was adjusted until full mixing of the water-soy material blend was feasible. The corresponding mass ratios are summarized in Table I. The KMnO_4 aqueous soy material mixture was stirred manually with a spatula until the mixture was homogenous (at least 5 min). The mixture was then dried at room temperature and < 20% RH and milled as described previously.

Chemical Composition. The analysis of the ash, cellulose, hemicellulose, lignin, and fat content for the soy materials was carried out according to AOAC methods and performed by Agri-Food Laboratories, Guelph, Canada. The ash content was determined by the AOAC 942.05 method, lignin by the ANKOM filter bag modified method of AOAC 973.18, protein content by the combustion method AOAC 990.03 and oil content by the AOAC 920.39 method. Cellulose was obtained by subtracting lignin from acid detergent fiber (ADF). Hemicellulose was obtained by subtracting ADF from neutral detergent fiber (NDF). The chemical composition of the soy materials before their treatment is presented in Table II.

Composite Preparation

Extrusion. Coupling agents (2.5 wt %), listed in Table III, were investigated for the selection of the best and worst coupling agent when preparing composites with 30 wt % soy material and 0.5 wt % Irganox 1010 (antioxidant).

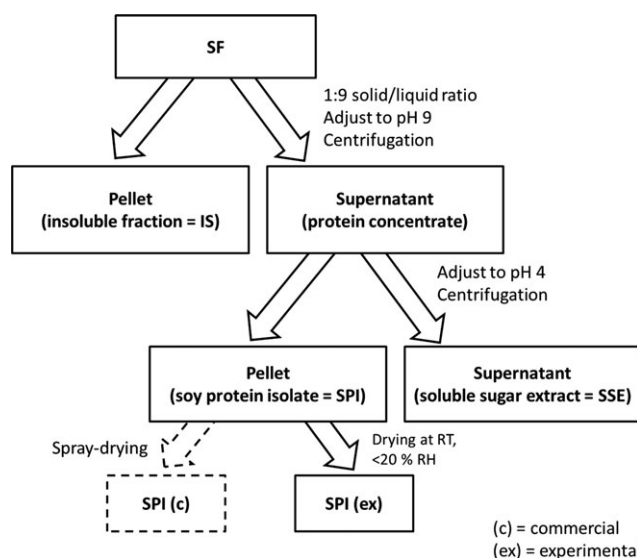


Figure 1. Diagram illustrating soy flour (SF) processing and the production of the water insoluble fraction (IS), acid precipitated soy protein isolate (SPI) and the water soluble sugar extract (SSE).

Table II. Chemical Composition of Soy Materials Before Treatment

Material	Protein (Nx6.25) (wt %)	Ash (wt %)	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)	Fat (wt %)	Other ^a (%)
SF	47.6	6.2	6.9	1.5	0.03	1.5	36.3
IS	45.9	N/A	10.4	10.2	6.0	N/A	27.5
SPI (c) ^b	<90.0	<5.0	N/A	N/A	N/A	4.0	1.0
SH	12.6	4.5	32.1	23.7	7.5	N/A	19.7

^aOther are mainly sugars other than cellulose and hemicellulose (e.g., pectin, starch); ^bReported values obtained from ADM.²⁶

Two sets of extrusion conditions were considered in this work to produce different quantities of composite materials. The single screw extruder was selected because a larger volume could be produced for the pre-extrusion of the PP material. The twin screw extruder was selected to produce small batches (~ 100 g) of individual composites. The composites containing different types of coupling agents and the polypropylene matrix were pre-extruded with the selected coupling agent and 0.5 wt % Irganox 1010 in a Haake MiniLab twin-screw micro compounder (Thermo Electron Corporation, USA) at 190°C and 40 rpm. For all other composites, the polypropylene blend was first extruded with 0.5 wt % Irganox 1010 at 190°C and 90 rpm in a Haake Rheomex 252 single-screw extruder with Haake Rheocord 90 Fisons (Thermo Electron Corporation, USA) and pelletized with a Berlyn pelletizer Model HVI (The Berlyn Corporation, USA). The compounding of the composites was then conducted with a Haake MiniLab twin-screw micro compounder (Thermo Electron Corporation, USA) operated at 190°C and 40 rpm.

Injection Molding. The extruded pellets were pressed into bars by using an injection molding apparatus from Ray-Ran. The barrel temperature was set at 190°C and the mould temperature at 50°C. The dimensions of the bars were according to ASTM D790 and D256 (length 63.5 ± 0.2 mm, width 12.7 ± 0.2 mm, depth 3.3 ± 0.2 mm).^{32,33}

Annealing and Conditioning. Annealing was performed to remove the stress of the composite and to provide uniform heating and cooling conditions for the consistent crystallization of the polymer matrix. Annealing was achieved by placing the bars in an oven (5890A GC, Hewlett Packard, USA) with an initial temperature of 31°C and 10°C/min heating rate until the final temperature of 151°C was reached. The final temperature was kept constant for 10 min before cooling to room temperature.

After annealing, the bars were left at least 48 h in an environmental chamber (model MLR-351H, Sanyo Electric, USA) at 50% RH and 23°C.

Composite Testing

Three-Point-Bending (ASTM D790). The testing was performed after annealing and conditioning of the bars. A flexural property instrument (Actuator model 120Q1000, TestResources, USA), was used at 1.335 mm/min crosshead speed, 65 mm deflection, 50 mm span. For each composite type, at least five samples were tested and an average was calculated with the corresponding standard deviation. The reported flexural strength is the maximum point of the stress/strain curve. The flexural modulus represents the slope of the first linear portion of the stress/strain curve.

Table III. Coupling Agents Used for Soy Composites

Coupling agent (manufacturer, location)	Composition	Maleic anhydride (MAH) content ^a
Licocene 1602 (Clariant International Ltd., Switzerland ²⁷)	PP copolymer	N/A ^b
Licocene 1332 TP (Clariant International Ltd., Switzerland ^{27,28})	PP, MAH grafted (low), low crystallinity	18 mg KOH/g
Licocene 3262Si (Clariant International Ltd., Switzerland ^{27,28})	PP with high degree of grafted comonomer: Trimethoxy vinyl silane	-
Licocene 6252 (Clariant International Ltd., Switzerland ²⁷)	PP, MAH grafted	38–45 mg KOH/g ^c
Priex 20097 (Addcomp Holland BV, Netherland ²⁹)	PP homopolymer, MAH	Free Maleic Anhydride: <50 mg/kg (Solvay method) Grafted Maleic Anhydride: 0.45% (Solvay method)
Orevac CA100 (Arkema Inc., USA ³⁰)	PP with high MAH content	High
Fusabond 353D (DuPont, USA ³¹)	PP with very high MAH grafting	Very high

^aMaleic anhydride content according to data sheet provided by manufacturer; ^bN/A, no data available; ^cKOH/g = mass of potassium hydroxide (KOH) required to neutralize one gram of maleic anhydride (acid number).

Table IV. Effect of Coupling Agent on the Notched Izod Impact Strength, Flexural Strength, and Flexural Modulus of Composites (\pm SD, $n \geq 5$) Containing 30 wt % SF, 0.5 wt % Irganox 1010 (Antioxidant)

Coupling agent	Notched Izod impact (J/m)	Change (%) ^a	Flexural strength (MPa)	Change (%) ^a	Flexural modulus (MPa)	Change (%) ^a
PP blend	50.0 \pm 1.8	-	45.4 \pm 2.5	-	1124.7 \pm 57.0	-
None (untreated SF)	20.3 \pm 0.9	0	36.4 \pm 2.5 ^b	0	1402.8 \pm 97.9	0
Licocene 1602	19.1 \pm 0.5 ^b	-5.9	37.7 \pm 2.0	3.6	1463.8 \pm 53.0	4.3
Licocene 1332	18.5 \pm 3.2 ^b	-8.9	38.1 \pm 0.6	4.7	1408.1 \pm 31.9	0.4
Licocene 3262Si	21.6 \pm 1.4 ^b	6.4	38.0 \pm 1.3	4.4	1426.4 \pm 75.3	1.7
Licocene 6252	20.4 \pm 3.6	0.5	42.0 \pm 1.3	15.4	1607.1 \pm 79.1 ^b	14.6
Priex 20097	21.0 \pm 2.9	3.4	42.4 \pm 1.4 ^b	16.5	1438.1 \pm 137.6	2.5
Orevac CA100	21.9 \pm 0.8 ^b	7.9	41.4 \pm 1.1	13.7	1420.6 \pm 42.5	1.3
Fusabond 353D	21.1 \pm 2.6	3.9	42.4 \pm 1.3 ^b	16.5	1498.8 \pm 91.6	6.8

^aChange relative to SF with no coupling agent. PL, palisade layer; ^bSignificance at $\alpha = 0.05$ when compared with composites with SF and no coupling agent

Notched Izod Impact (ASTM D256). After notching (notch cutter XQZ-I, Chengde Jinjian Testing Instrument, China), annealing and conditioning, the bars were tested for Izod impact strength. A monitor impact tester model 43-02-01 and hammer 0-1 x 0.01 ft-lbs, TMI #43-0A-03 (TestResources, USA) was used and operated at 50 % RH and 23 °C. For each composite type, at least five samples were tested and an average was calculated with the corresponding standard deviation.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was used for the analysis of crystallinity and the melting and crystallization peaks of the composites. DSC was performed in the dynamic mode with the differential scanning calorimeter Q2000 (TA Instruments – Waters LLC, USA). Approximately 5 mg of the composite material was placed in aluminum Tzero™ pan and heated in a nitrogen purged chamber (50 mL/min) from 35 to 200 °C at a rate of 10 °C/min. The analysis of the data (heat flow [W/g] vs. temperature [°C]) was carried out with the software Universal Analysis 2000 4.5A and the linear integration method (TA Instruments – Waters LLC, USA). The area under the first peak represented the enthalpy of the crystallization of the composite which was used to estimate the degree of crystallinity of polypropylene in the composite. The degree of crystallinity was estimated from the ratio between the measured crystallization enthalpy adjusted to 70 wt % polypropylene content and the published crystallization enthalpy of pure polypropylene (209 J/g).³⁴

Field Emission Scanning Electron Microscopy (FESEM). Fractured samples from Izod impact testing were gold coated in argon with a gold coating unit Desk II (Denton Vacuum, USA). Electron microscopy imaging was obtained with the Gemini Leo 1550 FESEM (Carl Zeiss AG, Germany) and with EDAX Genesis 5.2 (Ametek, USA). The working parameters for the FESEM were 12 kV and the secondary electron signal (SE2).

Statistical Analysis

The *t*-test was used for data analysis of significances between mean values of set of samples. The confidence interval was determined at a significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSION

The individual and combined contribution of coupling agent and soy treatment on the notched Izod impact and flexural properties for SF composites (30 wt % soy flour 0.5 wt % of Irganox 1010) were investigated. The relationship between impact strength and flexural modulus was evaluated. An initial screening of potential coupling agents was completed for untreated soy flour. A subsequent analysis was conducted for SF composites with the least and most favorable coupling agents and autoclave and potassium permanganate soy treatment. Their mechanical properties will be discussed in the context of composite morphology and crack propagation. The contribution of the two major constituents of soy flour, proteins as soy protein isolate (SPI) and carbohydrates as soy hulls (SH) was also evaluated.

Effect of Coupling Agents on the Mechanical Properties of Soy Flour Composites

The effect of coupling agents on the mechanical properties of soy flour composites is reported in Table IV. All composite materials showed impact strength within a narrow range, between 18.5 and 21.9 J/m. Significantly different impact properties ($\alpha = 0.05$) were observed when Licocene 1602, Licocene 1332, Licocene 3262Si, and Orevac CA100 was added compared to SF composites with no coupling agent (20.3 \pm 0.9 J/m). The most significant increase in impact strength (8% when compared to no coupling agent addition) was observed for the SF composite material prepared with Orevac CA100 (21.9 J/m) whereas the most significant decrease in impact strength (9% when compared to no coupling agent addition) was observed for the SF composite material prepared with Licocene 1332 (18.5 J/m). Both coupling agents are maleic anhydride grafted polypropylene but developed for different applications. Orevac CA100 was developed for composites with agricultural fillers³⁰ whereas Licocene 1332 was developed for adhesives and emulsions.²⁷ Priex 20097 and Fusabond 353D are also maleic anhydride coupling agents developed for improving the compatibility between agricultural fillers and polyolefins. The positive effect of these two coupling agents translated in the highest increase

Table V. Notched Izod Impact Strength, Flexural Strength, and Flexural Modulus of Soy-Polypropylene Composites (\pm SD, $n \geq 5$) Containing Combinations of Treated SF and Coupling Agents

Composite material	Notched Izod impact (J/m)	Change (%)	Flexural strength (MPa)	Change (%)	Flexural modulus (MPa)	Change (%)
SF	19.8 \pm 0.6	0 ^a	34.4 \pm 0.4	0 ^a	1173.1 \pm 24.1	0 ^a
SF (auto)	18.0 \pm 0.5 ^c	-9.1 ^a	38.8 \pm 4.4 ^c	12.8 ^a	1553.4 \pm 207.0 ^c	32.4 ^a
SF (KMnO ₄)	22.6 \pm 0.6 ^c	14.1 ^a	39.0 \pm 1.6 ^c	13.4 ^a	1445.6 \pm 73.1 ^c	23.2 ^a
SF (auto) + Licocene 1332	19.7 \pm 0.6	-0.4 ^b	38.7 \pm 1.0	12.5 ^b	1457.9 \pm 88.1	24.3 ^b
SF (auto) + Orevac CA 100	21.3 \pm 0.6 ^c	7.6 ^b	43.8 \pm 1.1 ^c	27.3 ^b	1573.8 \pm 81.7 ^c	34.2 ^b
SF (KMnO ₄) + Licocene 1332	21.1 \pm 0.2 ^c	6.7 ^b	33.7 \pm 0.9	-2.0 ^b	1237.6 \pm 76.1 ^c	5.5 ^b
SF (KMnO ₄) + Orevac CA 100	20.6 \pm 1.0	4.1 ^b	42.5 \pm 0.9 ^c	23.5 ^b	1465.9 \pm 117.4	25.0 ^b
SF (KMnO ₄ , auto)	20.7 \pm 0.6	4.4 ^b	31.0 \pm 0.5 ^c	-9.9 ^b	1233.5 \pm 38.4 ^c	5.1 ^b
SF (auto, KMnO ₄)	17.7 \pm 1.1 ^c	-10.5 ^b	36.3 \pm 0.7	5.5 ^b	1392.4 \pm 85.6	18.7 ^b
SF (KMnO ₄ & auto)	19.3 \pm 1.8	-2.3 ^b	34.7 \pm 0.7	0.9 ^b	1342.1 \pm 37.2	14.4 ^b

^aChange relative to untreated SF; ^bChange relative to the treated SF with no coupling agent; ^cStatistical significance at $\alpha = 0.05$.

of the flexural strength, 16.5%, when compared to SF composite with no coupling agent (36.4 ± 2.5 MPa). The flexural modulus for the SF composites prepared with coupling agents ranged between 1408 MPa (Licocene 1332) and 1607 MPa (Licocene 6252), the latter being a significant increase (14.6%) compared to SF composite material with no coupling agent addition.

On the basis of this preliminary screening, the least and the most favorable coupling agent for SF polypropylene composites, Licocene 1332 and Orevac CA100, were selected for further study when combined with soy flour subjected to autoclave and potassium permanganate treatment.

Effect of Soy Flour Treatment on the Mechanical Properties of Composites

Composites with soy flour subjected to potassium permanganate and autoclave treatment were prepared with no coupling agent but with the addition of 0.5 wt % Irganox 1010 as antioxidant. The impact strength, flexural strength, and flexural modulus properties are presented in Table V.

The lowest impact strength was 18.0 J/m for the SF (auto) composites. The highest impact strength was 22.6 J/m for the SF (KMnO₄) composites, corresponding to an increase of 14.1% when compared to the untreated SF composites (19.8 ± 0.6 J/m). The lower impact strength for the SF (auto) composites is most likely due to the increased hydrophilicity of the soy material (increased rate of water absorption³⁵) which could lower its compatibility with the hydrophobic polypropylene matrix. The notable impact strength increase of the SF (KMnO₄) composites could be related to changes of the soy material surface properties, namely the lower polar surface energy component.³⁵ Potassium permanganate is also known to modify hydroxyl groups of polymers creating initiation points for graft copolymerization and reducing the hydrophilic surface properties.^{16,36}

The flexural strength and moduli of elasticity increased for all composites prepared with treated SF when compared to composites prepared with untreated SF (34.4 ± 0.4 MPa). The SF (auto) composite showed the highest increased flexural modulus (at least 32%) when compared to the composite with untreated

SF. The SF (KMnO₄) composite flexural modulus increased by at least 23% when compared with untreated SF. The SF (KMnO₄) composite was the only composite where all properties improved simultaneously, suggesting the development of an ordered multiscale structure.

Effect of Soy Flour Treatment and Coupling Agent on the Mechanical Properties of Composites

The effect of maleic anhydride coupling agent addition (Licocene 1332 and Orevac CA100) on the impact and flexural properties of composites prepared with SF subjected to autoclave treatment [SF (auto)] or potassium permanganate treatment [SF (KMnO₄)] is presented in Table V.

Composites with SF (auto) and maleic anhydride coupling agent addition showed higher impact strength when compared to SF (auto) and no coupling agent. The highest impact strength increase was obtained for SF (auto) with the addition of Orevac CA100 (18.3% compared to SF (auto) and no coupling agent addition). Flexural strength and flexural modulus improved only for SF (auto) composite with Orevac CA100 addition when compared with SF (auto) and no coupling agent addition.

In contrast, the impact strength of SF (KMnO₄) composites decreased by nearly 8.8% with the addition of maleic anhydride coupling agent when compared to SF (KMnO₄) composites with no coupling agent addition. Coupling agent addition for SF (KMnO₄) composites had opposing effects on the flexural strength which decreased with Licocene 1332 addition but increased with Orevac CA100 addition. The impact and flexural properties of composites prepared with sequential autoclave and potassium permanganate SF treatment decreased when compared to the composites prepared with SF produced and individual treatments, SF (KMnO₄) and SF (auto). The composites prepared with SF subjected to combined autoclave and potassium permanganate treatments and without intermediate drying step, (SF (KMnO₄ + auto), showed similar impact strength and flexural strength but increased flexural modulus when compared with composites with SF and no treatment.

Table VI. Notched Izod Impact Strength, Flexural Strength, and Flexural Modulus of Composites (\pm SD, $n \geq 5$) Containing 30 wt % IS, SPI, or SH with and without Autoclave or Potassium Permanganate Treatment

Composite material	Notched Izod impact (J/m)	Change (%) ^a	Flexural strength (MPa)	Change (%) ^a	Flexural modulus (MPa)	Change (%) ^a
IS	19.2 \pm 1.0 ^b	0	32.1 \pm 0.8 ^b	0	1155.2 \pm 39.7 ^b	0
IS (KMnO ₄)	20.0 \pm 0.8	4.2	37.4 \pm 0.6 ^b	16.5	1327.1 \pm 48.8	14.9
SPI (c)	19.4 \pm 0.3 ^b	0	34.4 \pm 0.9	0	1452.1 \pm 48.1 ^b	0
SPI (auto)	19.5 \pm 1.0	0.5	32.2 \pm 0.6 ^b	-6.4	1154.2 \pm 24.1 ^b	-20.5
SPI (KMnO ₄)	21.2 \pm 1.6	9.3	33.6 \pm 0.3 ^b	-2.3	1193.5 \pm 18.4 ^b	-17.8
SH	21.7 \pm 0.6 ^b	0	34.3 \pm 0.8	0	1188.1 \pm 18.7 ^b	0
SH (auto)	22.0 \pm 0.5 ^b	1.4	37.4 \pm 0.6 ^b	9.0	1327.1 \pm 48.8	11.7
SH (KMnO ₄)	20.7 \pm 0.7	-4.6	36.2 \pm 0.5	5.5	1276.9 \pm 35.4	7.5

^aChange relative to the given soy material with no treatment; ^bStatistical significance $\alpha = 0.05$.

Maleic anhydride coupling agents, developed for agricultural composite materials, will bind to the hydrophilic groups at the surface of the agricultural materials and to the hydrophobic groups of the polymer matrix³⁷ thus providing improved mechanical properties. As the mechanical properties of soy flour after autoclave treatment and maleic anhydride addition improved, one can suspect increased hydrophilic group content at the surface of soy flour after autoclave treatment. The specificity of the maleic anhydride coupling agent efficiency and application target was confirmed where Orevac CA100, developed specifically for agricultural materials and polyolefins, showed the most pronounced positive effect.³⁰ The inefficiency of Licocene 1332 as coupling agent may be due to the different application target or the reduced hydroxyl group content caused by the addition of Mn³⁺ functional groups during the potassium permanganate treatment.^{16,38,39}

Effect of Soy Constituents on the Mechanical Properties of Composites

This work was performed to investigate the impact of the two main constituents (carbohydrates and proteins) of soy flour and study their changes when subjected to the different treatments. Composites were prepared with soy materials representing the major constituents of the soy flour, soy protein isolate (SPI) as protein constituent and soy hulls (SH) as carbohydrate constituent, and subjected to potassium permanganate treatment or autoclave treatment (Table VI). The most significant improvement of the impact strength was observed for the composite with SPI (KMnO₄), 9.3% compared to composites with SPI and no treatment. In contrast, the impact strength of composites with SH (KMnO₄) decreased by 4.6 % when compared to composites with SH and no treatment. The autoclave treatment for SPI and SH showed minor improvement of the composite impact properties when compared to composites with the corresponding untreated soy material (0.5 % and 1.4 % respectively). The flexural properties decreased more substantially for composites with SPI (auto) (6.4 % in flexural strength and 20.5 % in flexural modulus) when compared to composites with untreated SPI. Improved flexural properties were obtained only for the SH composites and the two treatments and IS (KMnO₄). The flex-

ural properties of the IS (KMnO₄) composites showed improved flexural strength up to 16.5 % and improved flexural modulus up to 14.9 %. This improvement may reflect the higher oxidation achieved during the KMnO₄ treatment conducted in alkaline conditions.⁴⁰ But differences in surface oxidation of the soy materials after KMnO₄ treatment could not be distinguished by FTIR analysis (data not shown).

Melting Behavior and Crystallinity

The crystallization and melting behavior of the composite materials was studied by DSC analysis (Table VII). The melting peak of the pure polypropylene blend was at 163.1°C and its degree of crystallinity was 58%. The melting peak of the soy polypropylene composite materials ranged from 159.0°C (SF) to 163.1°C [SPI (auto)]. The crystallization peak ranged from 116.8°C (IS) to 121.3°C [SPI (KMnO₄)]. The range of the degree of crystallinity of the soy polypropylene composite materials was quite narrow, 45.0% [SF (Orevac CA100)] to 49.9% [SPI (KMnO₄)], and lower than for the pure polypropylene blend. The degree of crystallinity of SF composites increased with Licocene 1332 addition but decreased with Orevac CA100 addition. Licocene 1332 addition to the SF (KMnO₄) and SF (auto) composites decreased the crystallinity (10 and 20%, respectively) when compared with untreated SF composites with Licocene 1332. In contrast, Orevac CA100 addition increased the degree of crystallinity for the SF (KMnO₄) and SF (auto) composites when compared with untreated SF and SF with Orevac CA100 composites. The high degree of crystallization of SF (auto) was unexpected due to its low impact properties and would need additional work to evaluate potential structural changes. The highest crystallization peak temperature was observed for all SPI composites with and without treatments which may be due to an increased crystal size of the major crystal fraction present in the composite materials. A comparison of the crystallization behaviour to the polar energy properties of the soy materials (data not shown) indicates that the highest degree of crystallinity was observed for the soy material with the lowest polar surface energy.⁴¹

Table VII. Melting and Crystallization Properties of Soy-Polypropylene Composite Materials

Composite material	Melting		Crystallization		Degree of crystallinity (%)
	Peak max. (°C)	ΔH_m (J/g)	Peak max. (°C)	ΔH_c (J/g)	
PP blend	163.1	119.4	119.5	120.8	57.8
SF (Orevac CA100)	159.6	65.8	118.2	65.9	45.0 ^a
SF (Licocene 1332)	160.6	82.1	117.8	70.5	48.2 ^a
SF	159.0	69.5	117.1	68.4	46.7
SF (auto)	159.3	72.4	117.8	71.9	49.2 ^a
SF (auto) + Orevac CA100	159.7	72.7	118.9	71.1	48.6 ^a
SF (auto) + Licocene 1332	160.0	56.4	115.4	56.4	38.5 ^a
SF (KMnO ₄)	159.3	70.8	117.5	70.1	47.9
SF (KMnO ₄) + Orevac CA100	160.9	73.3	120.0	70.9	48.4
SF (KMnO ₄) + Licocene 1332	159.9	63.5	116.3	63.6	43.5 ^a
IS	160.0	72.5	116.8	69.6	47.6
IS (KMnO ₄)	161.8	71.4	117.6	69.7	47.6
SPI	160.9	70.0	120.3	69.3	47.4
SPI (auto)	163.1	76.3	120.8	71.0	48.5 ^a
SPI (KMnO ₄)	160.6	73.5	121.3	72.9	49.9 ^a
SH	159.4	72.0	117.3	69.1	47.2
SH (auto)	160.6	71.9	118.0	70.0	47.9
SH (KMnO ₄)	160.9	67.7	117.2	69.1	47.2

^aStatistical significance $\alpha = 0.05$.

Correlation between Soy-Polypropylene Composite Material Toughness and Strength

The Izod impact strength is presented according to flexural modulus (Figure 2) and protein content (Figure 3). Composite materials will typically show an opposite relationship between impact and flexural properties such that by increasing one property, the other property will decrease and vice versa.^{24,42} This opposite effect represents the inverse correlation between toughness and strength. Such a relationship was also observed previously for synthetic polymers, polyesters, and PTE.^{42,43} Therefore a trade-off between toughness and elasticity is needed

when developing the most suitable material for a target application. Such an inverse correlation is not present in some natural materials such as bones or chitin insect cuticles which were explained by their multiscale structure.¹⁹ Most soy polypropylene composite materials investigated in this study, showed an inversely proportional correlation between the Izod impact strength and the flexural modulus with the exception of two SF composites, SF (KMnO₄) and SF (auto) with Orevac CA100 (Figure 2). These two SF composite materials showed improved Izod impact strength with increased moduli of elasticity. Further work would be needed to identify if a multi-level ordered structure of the composite material was developed. In contrast, no

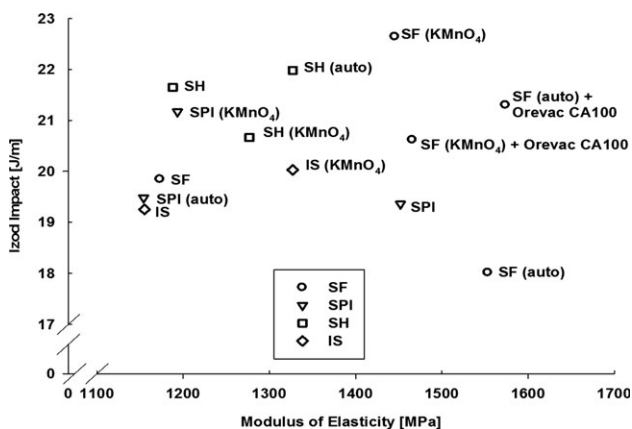


Figure 2. Correlation between Izod impact and flexural modulus of soy-polypropylene composite materials with untreated, KMnO₄ and autoclave treated SF, SPI, SH, and IS.

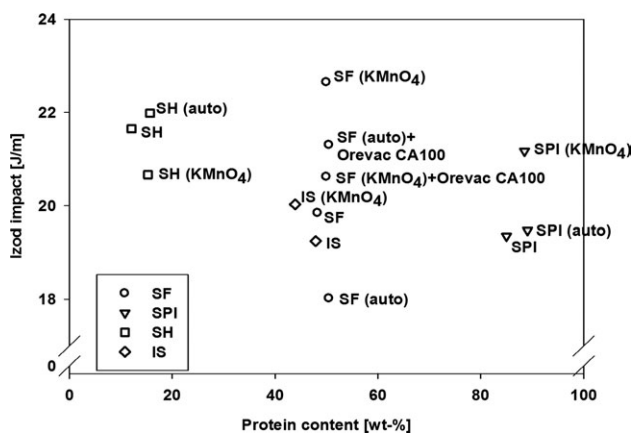


Figure 3. Izod impact strength of composite materials vs. protein content of corresponding soy materials.

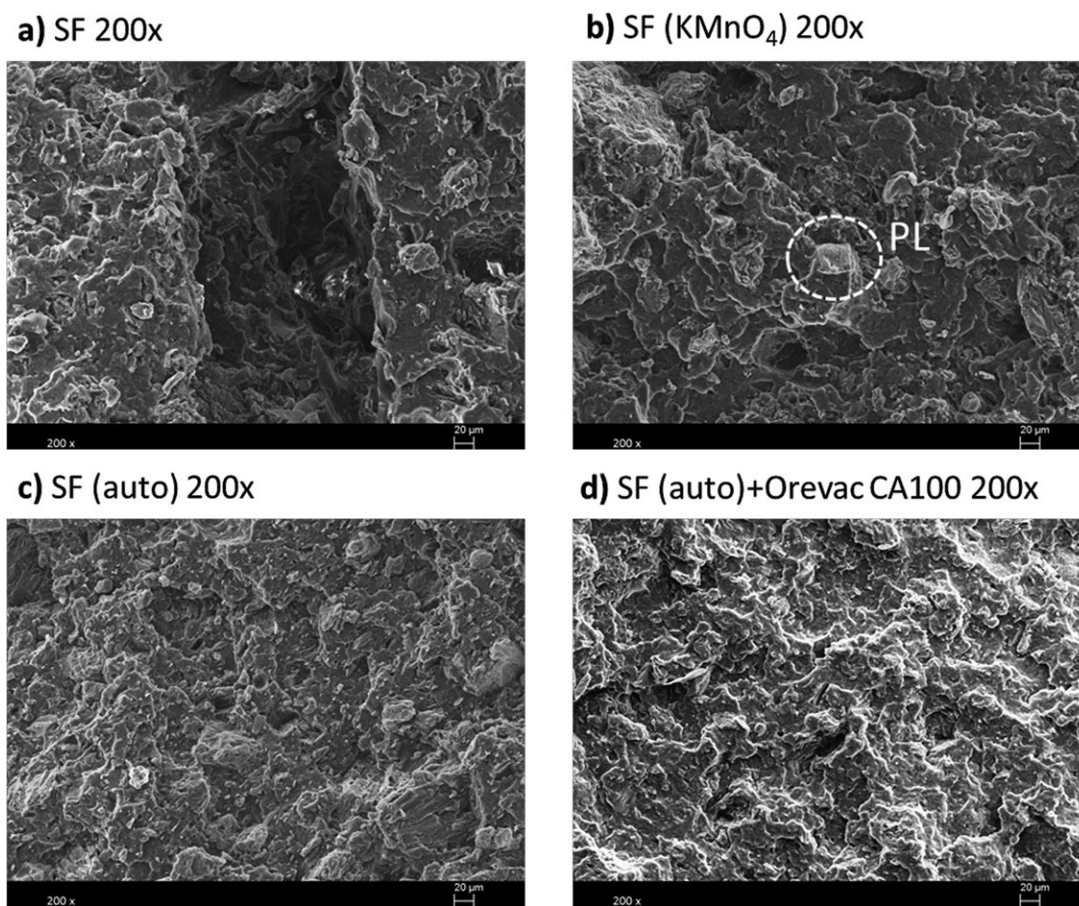


Figure 4. Low magnification FESEM images (200x magnification) of the fractured surface produced after impact testing of soy-polypropylene composites formulated with (a) SF, (b) SF (KMnO_4) (c) SF (auto), (d) SF (auto) + Orevac CA100. PL, palisade layer.

correlation was observed between the Izod impact strength and protein content (Figure 3).

Morphology of the Composites after Impact Testing

FESEM of the fractured surface produced after impact testing is shown in Figure 4 (low magnification) and Figure 5 (high magnification). The surface of SF and SF (auto) [Figure 4(a,c)] showed distinct voids separating the soy materials from the matrix. The surface of SF (KMnO_4) [Figures 4(b), 5(b,d)] showed soy flour partially attached to the matrix as well as cracks between the soy flour and the polypropylene matrix. The surface of the soy flour (especially the palisade layer which has a fibrous structure) had a smoother appearance when compared to the surface of SF [Figures 4(a) and 5(a)], SF (auto) [Figures 4(c), 5(c,e)]. A comparison of SF (auto) (Figures 4(c), 5(c,e)) and Orevac CA100 (Figures 4(d) and 5(f)) to the other materials revealed much smoother SF surface with most of the soy flour fully embedded in the matrix.

Since soy materials were used directly after potassium permanganate treatment, the presence of crystals in these materials was evaluated. No crystals were detected for the composites prepared with soy material and KMnO_4 treatment which suggests negligible residual KMnO_4 . Sodium chloride crystals were previously detected in soy flour-polypropylene composites with SEM.¹⁸

Proposed Crack Propagation Mechanism

Cracks in a material will appear in response to mechanical stresses. In the context of composite materials, cracks will develop in the least resistant domain of the material. Accordingly, three well-established crack propagation cases for dispersed phase polymer composite materials are shown in Figure 6: (a) through the matrix, (b) through the dispersed phase, and (c) through the interface. The mechanical properties will change according to the interfacial bond strength between the dispersed phase and the continuous polymer phase.⁴⁴ The interface can be modified by chemical or mechanical treatments altering the mechanical properties of the composite material. For example, the impact strength depends on the matrix-interface characteristic and may increase according to the type of dispersed phase (filler or fiber), the dispersed phase loading, its orientation or origin.⁴⁴ When the dispersed phase-matrix interface is very strong, the matrix becomes the weakest domain of the composite such that cracks will propagate through this domain leaving the dispersed phase and the interface intact (case a). When the bonding between the dispersed phase and matrix is strong, the dispersed phase will break before detachment from the matrix (case b). If the bonding between the dispersed phase and matrix is poor, the dispersed phase will detach from the matrix when stress is applied (case c).

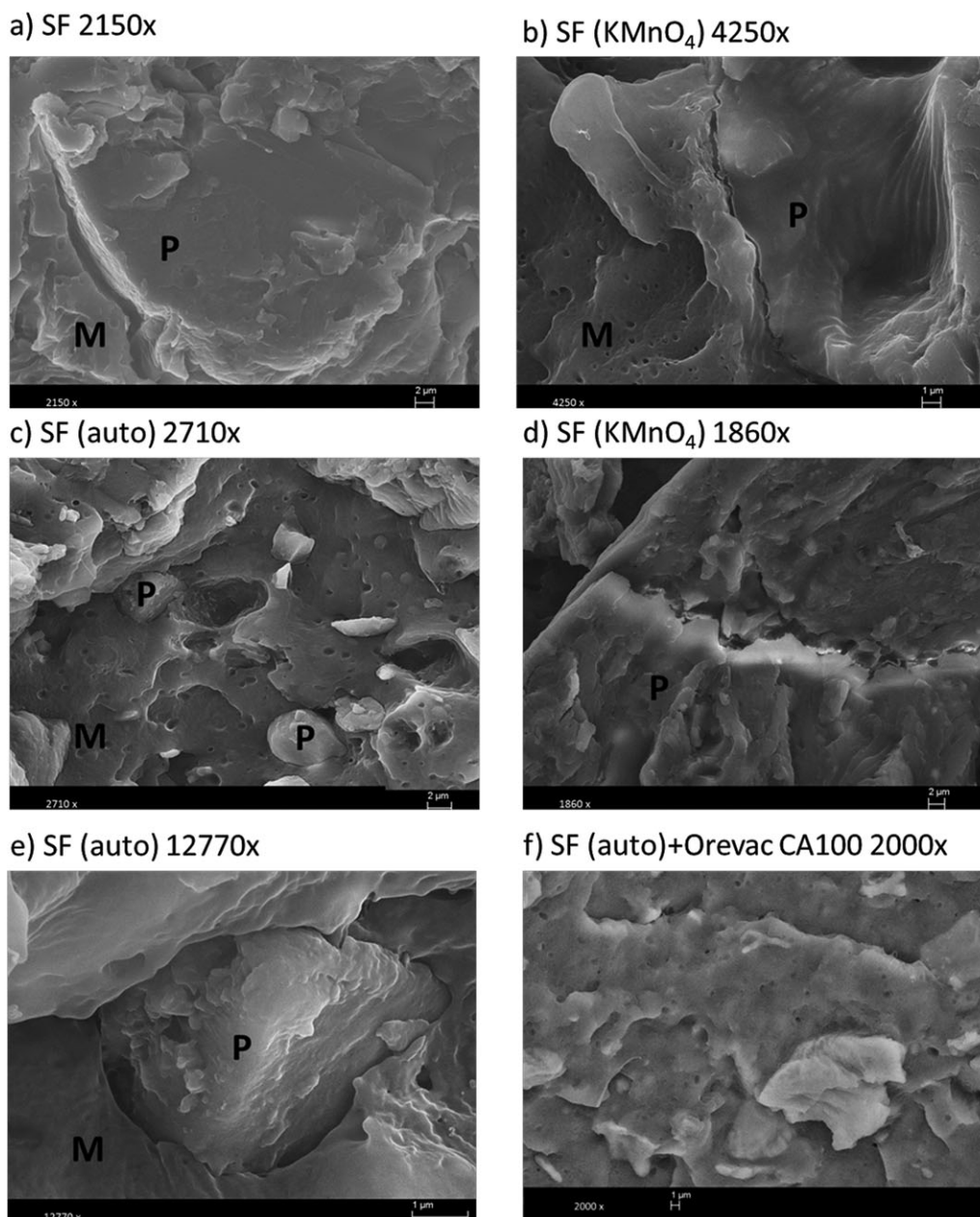


Figure 5. High magnification FESEM images of the fractured surface produced after impact testing of the soy-polypropylene composites formulated with (a) SF (2150x), (b) SF (KMnO₄) (4250x), (c) SF (auto) (2710x) (d) SF (KMnO₄) (1860x), (e) SF (auto) (12770x), (f) SF (auto) + Orevac CA100 (2000x). P, particle; M, matrix.

Comparing the FESEM images presented in Figures 4 and 5, different crack propagation mechanisms could be identified for a given soy-polypropylene composite material. SF composites showed mostly detachment between the soy material and matrix (case c) whereas SF (KMnO₄) composites displayed partial soy material-matrix bonding that was associated with improved impact strength. SF (KMnO₄) composite materials also showed some cracks through the soy material (case b). An example for good interfacial bonding was the SF (auto) + Orevac CA100 composite material which showed crack propagation through the matrix (case a).

Yang et al. reported on coupling agent addition for rice husk-polypropylene composites,⁴⁵ bonding quality between the dispersed phase and the matrix and the presence of cracks at the interface.⁴⁵ Their work showed that cracks were located in the dispersed phase when 3% coupling agent was added.

Sailaja et al. studied polypropylene composites with 20% soy flour.⁴⁶ Without coupling agent, detachment between the soy flour dispersed phase and the polypropylene matrix was observed. After the addition of 6% coupling agent, the dispersion and interlocking of soy flour and matrix was improved.

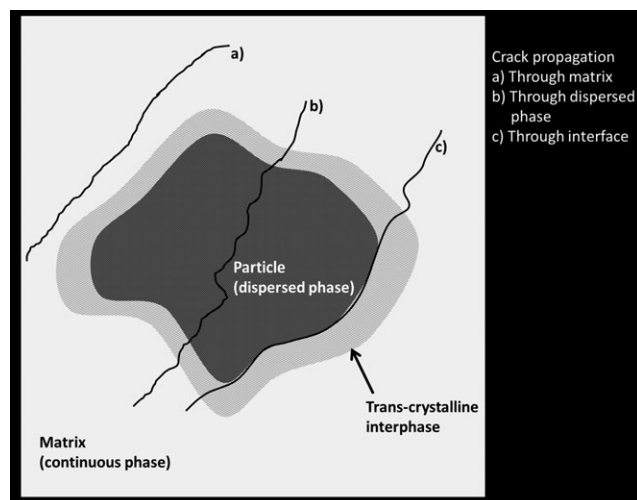


Figure 6. Schematic representation of different crack propagation mechanisms: (a) through matrix, (b) through dispersed phase, (c) through interface.

CONCLUSIONS

Soy flour (SF), obtained by milling soy meal to a particle size below 80 μm , was subjected to potassium permanganate and autoclave treatments. The treated soy flour was compounded with polypropylene with and without the addition of seven different coupling agents. Two maleic anhydride coupling agents (least and most favorable according to impact strength), Lico-cene 1332 and Orevac CA100, were selected for composite formulation with SF subjected to potassium permanganate or autoclave treatment. The addition of maleic anhydride coupling agent improved the impact strength for the SF (auto) composites but decreased for the SF (KMnO_4) composites. The positive effect of maleic anhydride coupling agent addition for SF (auto) composites could be due to the higher hydrophilicity of SF (auto) which may have enhanced its reactivity with maleic anhydride. The negative effect of maleic anhydride for SF (KMnO_4) composites could be due to the presence of reactive groups (Mn^{3+}) and the reduced hydroxyl content on the soy flour surface. Scanning electron microscopy imaging of the fractured composite surface, produced during impact testing, revealed different morphology and crack propagation mechanisms according to the type of treatment and/or maleic anhydride coupling agent. Even though the surface of SF (auto) with Orevac CA100 showed crack propagation through the matrix, indicating a very good dispersed phase-matrix bonding, the impact strength of SF (KMnO_4) was the highest. Nevertheless, both materials had unusual mechanical properties with simultaneous increase of the impact strength and flexural modulus. Since treatments affected more significantly the impact strength of SPI composites than SH composites, one can deduce that the treatments affected predominantly the protein fraction of soy flour.

KMnO_4 and autoclave treatments modified the soy materials by improving their compatibility with the polypropylene matrix [SF (KMnO_4)] or their reactivity with maleic anhydride coupling agent [SF (auto)] resulting in increased toughness and

strength of the composite materials. Further work is needed to understand the effect of maleic anhydride addition and its potential contribution to crystallization of the polypropylene matrix and the effect of the autoclave and KMnO_4 treatment on the soy materials.

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