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Elastomer modified polypropylene–polyethylene blends as matrices for wood flour–plastic composites ☆

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ABSTRACT

Blends of polyethylene (PE) and polypropylene (PP) could potentially be used as matrices for wood–plastic composites (WPCs). The mechanical performance and morphology of both the unfilled blends and wood-filled composites with various elastomers and coupling agents were investigated. Blending of the plastics resulted in either small domains of the minor phase in a matrix of major phase or a co-continuous morphology if equal amounts of HDPE and PP were added. The tensile moduli and yield properties of the blends were clearly proportional to the relative amounts of HDPE and PP in the blends. However, the nominal strain at break and the notched Izod impact energies of HDPE were greatly reduced by adding as little as 25% of the PP. Adding an ethylene–propylene–diene (EPDM) elastomer to the blends, reduced moduli and strength but increased elongational properties and impact energies, especially in HDPE-rich blends. Adding wood flour to the blends stiffened but embrittled them, especially the tougher, HDPE-rich blends, though the reductions in performance could be offset somewhat by adding elastomers and coupling agents or a combination of both.

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1. Introduction

Polymers are routinely combined to provide blends that better meet performance requirements or extend performance into new applications. Not surprisingly, there are many commercial examples of polymer blends/patents and reviews on the subject are readily available [1–3].

However, from a recycling perspective, the motivations are often different. It is technically difficult or uneconomical to separate certain combinations of plastics. For example, blends of polypropylene, polyethylene, and polystyrene often remain after various separation strategies have been applied to a plastics waste stream. Sometimes called the "light fraction" due to the low densities of the components, it is often difficult and uneconomical to completely separate these plastics [1]. The performance of these commingled blends is often well below those of the individual components due to incompatibility of the plastics in the blends, unfavorable morphologies, or contamination.

Because of their importance in recycling, various strategies of improving the performance blends containing polyethylene (PE) and polypropylene (PP) have been intensively investigated [4]. Though the miscibility of polymers depends strongly on molecular weight and structure, the great majority of polymers have limited miscibility with each other [5]. Even different PEs are often immiscible with each other despite chemical similarity [6]. It is hardly surprising then that polyethylene and polypropylene are usually immiscible and exist as separate phases when blended [7]. Complicating the interaction between PEs and PPs is the fact that both are semicrystalline plastics. Depending on specifics of polymer structure and the conditions under which they blended, they can cocrystallize, crystallize separately, or even exhibit epitaxy [5].

Adding small amounts of PE or PP to the other has been reported to yield some improvement in performance, in certain circumstances [7]. For example, small amounts of PE have been added to PP to improve low temperature impact properties. Other advantages have been found such as improved microcellular foaming of PE or PP when the two are blended [8]. However, the incompatibility of the PP/PE most often results in reduced performance. Though moduli and strength of the blends generally lies between those of the unfilled polymers, uncompatibilized blends often fail at low strains and generally have low impact performance, limiting their usefulness [5].

The morphology and performance of PP–PE blends is a function of a variety of variables including molecular structure, viscosity and elasticity ratios of the blend components, and additives such

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Table 1
Blend composition and mechanical property summary for the sequential compatibilization approach.

Blend	PE/PP ratio (%/%)	Plastic content (%)	EPDM (%)	WF (%)	MAPE (%)	MAPP (%)	MA–EPDM (%)	Tensile properties			Flexural properties		Izod impact properties	
								Tensile modulus (GPa)	Tensile yield stress (MPa)	Yield strain (%)	Flexural modulus (GPa)	Flexural strength (MPa)	Notched impact energy (J/m)	Reversed notch impact energy (J/m)
Unfilled blends														
1A	100/0	100	0	0	0	0	0	0.76 (0.01)[a]	20.9 (0.1)	10.8 (0.3)	0.56 (0.01)	20.2 (0.3)	125.8 (1.6)	NB[b] (–)
1B	75/25	100	0	0	0	0	0	1.09 (0.02)	25.2 (0.1)	9.6 (0.3)	0.82 (0.02)	26.2 (0.4)	35.3 (1.1)	NB (–)
1C	75/25	90	10	0	0	0	0	0.80 (0.02)	21.4 (0.2)	12.8 (0.4)	0.66 (0.02)	21.3 (0.5)	567.3 (9.0)	NB (–)
1D	50/50	100	0	0	0	0	0	1.44 (0.03)	30.6 (0.3)	8.4 (0.2)	1.11 (0.02)	34.6 (0.6)	34.3 (1.2)	NB (–)
1E	50/50	90	10	0	0	0	0	1.05 (0.02)	25.4 (0.2)	12.0 (0.3)	0.90 (0.01)	27.2 (0.3)	129.6 (8.1)	NB (–)
1F	25/75	100	0	0	0	0	0	1.56 (0.02)	34.8 (0.3)	7.5 (0.2)	1.43 (0.03)	42.7 (0.6)	30.0 (1.0)	748 (26)
1G	25/75	90	10	0	0	0	0	1.38 (0.03)	29.3 (0.2)	10.4 (0.3)	1.19 (0.01)	33.9 (0.2)	55.6 (6.7)	NB (–)
1H	0/100	100	0	0	0	0	0	2.06 (0.02)	38.2 (0.3)	6.7 (0.3)	1.74 (0.05)	50.1 (1.1)	28.2 (2.9)	635 (23)
Composite														
1I	100/0	70	0	30	0	0	0	2.82 (0.03)	21.4 (0.1)	3.1 (0.0)	1.80 (0.03)	31.0 (0.3)	48.4 (2.6)	79 (8)
1J	100/0	67	0	30	3	0	0	2.92 (0.07)	26.6 (0.5)	2.8 (0.2)	1.76 (0.03)	36.9 (0.5)	46.4 (1.7)	94 (7)
1K	75/25	70	0	30	0	0	0	3.34 (0.11)	23.1 (0.3)	2.4 (0.3)	2.21 (0.06)	35.9 (0.4)	44.1 (2.0)	73 (8)
1L	75/25	60	10	30	0	0	0	2.49 (0.16)	18.5 (0.1)	3.7 (0.1)	1.47 (0.09)	26.5 (0.2)	64.2 (3.6)	97 (10)
1M	75/25	67	0	30	3	0	0	3.33 (0.12)	26.1 (0.2)	2.2 (0.2)	2.10 (0.18)	37.0 (2.2)	40.5 (1.9)	68 (11)
1N	75/25	57	10	30	3	0	0	2.63 (0.08)	20.7 (0.2)	3.2 (0.2)	1.44 (0.01)	25.3 (0.3)	61.1 (2.6)	87 (6)
1O	75/25	60	0	30	0	0	10	2.26 (0.10)	25.0 (0.3)	3.9 (0.1)	1.36 (0.10)	30.6 (2.3)	71.9 (2.1)	160 (8)
1P	50/50	70	0	30	0	0	0	3.77 (0.05)	25.0 (0.7)	1.6 (0.1)	2.67 (0.07)	41.7 (0.6)	28.6 (1.5)	66 (5)
1Q	50/50	60	10	30	0	0	0	2.77 (0.08)	20.7 (0.1)	3.0 (0.1)	2.03 (0.07)	31.5 (0.5)	45.9 (2.0)	85 (7)
1R	25/75	70	0	30	0	0	0	3.90 (0.29)	28.3 (0.3)	2.0 (0.2)	3.04 (0.09)	47.1 (0.6)	26.5 (0.6)	71 (6)
1S	25/75	60	10	30	0	0	0	3.11 (0.08)	22.9 (0.3)	1.9 (0.3)	2.45 (0.06)	37.1 (0.9)	40.9 (2.1)	85 (5)
1T	25/75	67	0	30	0	3	0	4.02 (0.04)	36.2 (1.0)	2.7 (0.2)	3.05 (0.07)	58.6 (0.9)	24.4 (2.0)	92 (4)
1U	25/75	57	10	30	0	3	0	3.12 (0.06)	30.5 (0.2)	3.4 (0.1)	2.28 (0.04)	46.1 (0.4)	49.7 (1.3)	126 (12)
1V	25/75	60	0	30	0	0	10	2.71 (0.06)	26.9 (0.1)	2.9 (0.2)	1.95 (0.02)	37.2 (0.3)	52.7 (1.5)	124 (7)
1W	0/100	70	0	30	0	0	0	4.08 (0.09)	29.3 (0.9)	1.8 (0.3)	3.16 (0.05)	45.8 (0.7)	26.0 (2.3)	70 (7)
1X	0/100	67	0	30	0	3	0	4.16 (0.07)	39.0 (0.3)	2.0 (0.1)	3.13 (0.10)	60.8 (2.9)	24.7 (1.5)	87 (4)

[a] Numbers in parentheses are one standard deviation.
[b] NB means that the specimen did not break during the impact testing.

as compatibilizers [5]. If significantly different amounts of blend components are mixed, the minor phase is usually dispersed in a matrix of the major phase. In general, the size of the dispersed domains increases as more is added, with less mixing, more annealing, or slower cooling [5]. When nearly equal proportions of PE and PP are blended an interpenetrating morphology can result, which tends to improve properties albeit over a narrow compositional range.

Processing history has an especially strong influence on morphology and manipulating the multiphase structure of immiscible polymer blends is one approach to improving their performance. For example, new processing approaches have produced microlayered morphologies [9], interpenetrating networks [9], or in situ microfibrillar reinforcement [10–15]. If the morphology is carefully controlled, large improvements in performance can be achieved at optimal processing conditions but special equipment is often required and large improvements are found only over a limited compositional range and narrow processing conditions. Additionally, if the material is heated, the morphology can be altered and the performance decreased.

Several solid state methods have been used to improve compatibility of recycled plastics relying on processes such as ball milling [16,17], solid state sheet rolling [4], and solid state shear pulverization [18] to produce free radicals and generate compatibilizing copolymers [4]. Free radical initiators such as organic peroxides have also been added to PE–PP blends to generate macroradicals that recombine to form PE–PP copolymers and compatibilize the blend. When processing with peroxides, PE tends to crosslink but PP chain length usually degrades and monomers or coreactants have been investigated to suppress this PP degradation and promote formation of PE–PP copolymers [19]. Other researchers have used other compatibilizers such as diisocyanate-modified PE–PP copolymer [20]; maleated polypropylene/polyethylene with dodecane diamine, zinc acetate, or sodium hydrogenocarbonate [21]; or a neoalkoxy pyrophosphate titanate [22].

However, the use of elastomeric block or random copolymers and terpolymers are still the most commonly used compatibilizers for PE–PP blends because of their low cost, ease of use, and the reasonable performance balance of the resulting blend [23–26]. Compatibilization is achieved through incorporation of miscible or at least compatible segments of the copolymer molecules into the different phases, tying them together. The copolymer molecule can act as a bridge between the phases and transfer stress between them. The resulting blend has a finer and more stable morphology [27]. Ethylene–propylene (EPR) and ethylene–propylene–diene (EPDM) elastomers are used most often commercially due to their low cost.

Due to their elastomeric nature, modulus is reduced when these compatibilizers are added. Strength is also reduced while elongation at break and impact properties are increased. Crystallinity is often affected as well [5]. The viscosity, the proportion ethylene and propylene, and the crystallinity of the elastomer affect its performance in PE–PP blends. These elastomers show a slight preference for PE over PP [5]. A wide range of elastomer contents have been used in PE–PP blends depending on the desired balance of properties. The list of articles and patents over the last 40 years on EPR and EPDM copolymer compatibilized PE–PP blends is considerable and has been summarized by others [4,7].

Elastomers have also been used to modify the performance of filled polyolefins such as wood–plastic composites (WPCs) [28–31]. The chemical architecture of the elastomer influences how it functions in the composite. For example, it can toughen the matrix, usually by generating localized yielding rather than catastrophic failure [28]. A fine elastomer domain size (often less than 1 μm) is preferred [28]. Some elastomers (e.g., maleic anhydride modified EPDM) can partially or completely encapsulate filler particles such as wood flour reducing the stress concentrations created by the fillers [30,31] and improving filler–matrix adhesion and stress transfer.

However, little work has been performed on WPCs made with elastomer modified PP–PE blends and wood flour [32–34]. Developing such technology is particularly timely given the rapid growth of wood–plastic composite markets in the last decade as well as the public desire for better disposal methods for waste plastics and plant-based residues such as wood flour. WPCs are already a significant outlet for recycled films. This research was undertaken to provide baseline information on elastomer modified polyethylene–polypropylene blends as matrices for WPCs. Virgin plastics are used in this initial investigation as model materials to better control material variability.

2. Experimental

2.1. Materials

The HDPE used for this portion of the project was HD 6605, a HDPE homopolymer with a melt flow index of 5 g/10 min (ExxonMobil Chemical). The PP was Certene PHM-20AN, a homopolymer with a melt flow index of 20 g/10 min (Muehlstein and Co., Inc.). The wood filler was a nominal 40 mesh (420 μm) western pine wood flour from American Wood Fibers. The following additives were investigated.

An ethylene–propylene–diene (EPDM) elastomer, Royalene IM 7565, was used to compatibilize the PP and HDPE. Such elastomers have been show to be effective in improving impact and extensional properties at moderate cost. This specific elastomer is actually a 63:35 blend of EPDM and HDPE by weight [35]. The EPDM component, Royalene 580HT, is an ethylene/propylene (E/P) copolymer with an E/P ratio of 53/47, a broad molecular weight

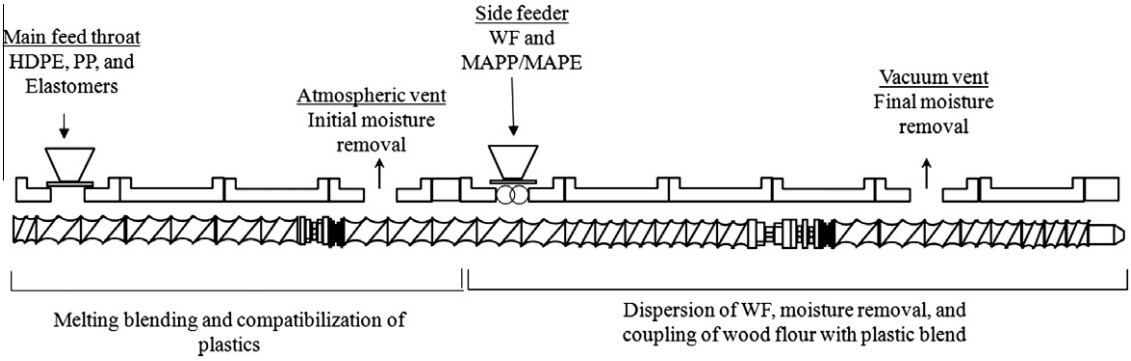

Fig. 1. Compounding approach for wood flour filled blends.

Table 2
Summary of high speed puncture tests for PE, PP, and their blends.

Blend	PE/PP ratio	Plastic content (%)	EPDM (%)	WF (%)	MAPE (%)	MAPP (%)	MA-SEBS (%)	Failure mode	Load at yield/ fracture (kN)	Deflection at yield/ fracture (mm)	Energy to yield/ fracture (kg m)
1A	100/0	100	0	0	0	0	0	Yield	1.139 (0.003)[a]	15.41 (0.12)	7.27 (0.07)
1B	75/25	100	0	0	0	0	0	Yield	1.120 (0.008)	14.56 (0.04)	6.82 (0.09)
1C	75/25	90	10	0	0	0	0	Yield	1.008 (0.004)	14.85 (0.05)	6.22 (0.05)
1D	50/50	100	0	0	0	0	0	Yield	1.111 (0.009)	14.64 (0.05)	8.91 (0.09)
1E	50/50	90	10	0	0	0	0	Yield	1.149 (0.014)	14.54 (0.10)	6.95 (0.12)
1F	25/75	100	0	0	0	0	0	Brittle fracture	0.590 (0.054)	7.55 (0.38)	1.80 (0.23)
1G	25/75	90	10	0	0	0	0	Yield	1.254 (0.024)	14.47 (0.07)	7.54 (0.20)
1H	0/100	100	0	0	0	0	0	Brittle fracture	0.330 (0.052)	4.71 (0.56)	0.63 (0.14)

[a] Numbers in parentheses are one standard deviation.

distribution, and a density of 0.86 g/cm^3. For the sake of brevity, this EPDM and HDPE blend is simply referred to as EPDM.

A maleated polyethylene (MAPE), Polybond 3009 from Chemtura Corporation, was used to improve bonding between the wood flour and plastic blend when HDPE-rich plastic blends were used as a matrix. The MAPE had a melt flow index of 5 g/10 min, and a maleic anhydride content of 1% by weight.

For PP-rich blends, a maleated polypropylene (MAPP), Epolene G-3015 from Eastman Chemical, was used to improve bonding between the wood flour and plastic blend. The MAPP had a number average molecular weight (M_n) = 24,800, weight average (M_w) = 47,000, and acid number of 15 mg KOH/g.

A second elastomer, a maleated EPDM elastomer, Royaltuf 485 from Chemtura Corporation, was also investigated as a coupling agent or compatibilizer for all three components. The maleated EPDM (MA–EPDM) had a maleic anhydride content of 0.5% and a specific gravity of 0.85.

2.2. Test matrix

The blends made are summarized in Table 1. Blends 1A–1H are the unfilled plastic blends at various weight ratios, with and without the EPDM compatibilizer and form a baseline for comparison with the composites. For composite blends with PE/PP ratios of 75/25 and 25/75, various compatibilizers are investigated including the EPDM elastomer, MAPE for high PE content formulations, MAPP for high PP content formulations, and a compatibilizer containing maleated anhydride, propylene, and ethylene segments (MA–EPDM). MA–EPDM elastomers have previously been investigated as a compatibilizer in PP–WF composites but not in wood flour composites with PE–PP blends [31]. Several selected composite blends with PP or PE only are included for comparison purposes.

2.3. Processing

Compounding of all blends was performed on a 32-mm twin screw compounding line (D-Tex, Davis Standard). The HDPE, PP and elastomeric compatibilizers all were in pellet form and were premixed in appropriate ratios prior to extrusion depending on the formulations listed in Table 1. This pellet mixture was then fed into the main feed throat and the materials were melted, blended, and compatibilized in the first part of the extruder (Fig. 1). The wood flour and MAPP or MAPE coupling agent (when used) were fed into the 5th zone of the extruder using a side feeder. The wood flour was subsequently dispersed and coupling agent was melted and blended into the mix to improve the adhesion between the plastic and wood flour. Any moisture vapor from the wood flour was removed by atmospheric and vacuum venting in the 4th and 9th stages, respectively. The molten blend was then forced through a strand die, cooled, and pelletized. A gravimetric feed system (SCHENK-AccuRate) was used to ensure accurate metering of all materials into the extruder in the proper proportions. Three loss-in-weight feeders were used: one for the premixed pellet mixture fed into the main feed throat, one for the wood flour fed into the side feeder, and one for the MAPE or MAPP pellets fed into the side feeder. A master controller (DG-2000 Group Controller, SCHENK-AccuRate) was used to gravimetrically control all feed rates. A temperature profile from 160 °C at the feed throat to 180 °C at the die was used for all formulations.

Table 3
Summary of high speed puncture test results at the incipient damage point for composites.

Blend	PE/PP ratio (%/%)	Plastic content (%)	EPDM (%)	WF (%)	MAPE (%)	MAPP (%)	MA–EPDM (%)	Load @ incipient damage (kN)	Deflection @ incipient damage (mm)	Energy required to initiate damage (J)
1I	100/0	70	0	30	0	0	0	0.280 (0.010)[a]	5.63 (0.21)	0.869 (0.062)
1J	100/0	67	0	30	3	0	0	0.226 (0.015)	4.84 (0.25)	0.583 (0.055)
1K	75/25	70	0	30	0	0	0	0.236 (0.010)	5.07 (0.05)	0.568 (0.170)
1L	75/25	60	10	30	0	0	0	0.284 (0.020)	6.26 (0.38)	0.875 (0.119)
1M	75/25	67	0	30	3	0	0	0.163 (0.014)	3.07 (0.37)	0.267 (0.058)
1N	75/25	57	10	30	3	0	0	0.246 (0.003)	5.59 (0.47)	0.659 (0.109)
1O	75/25	60	0	30	0	0	10	0.336 (0.031)	6.59 (0.36)	1.005 (0.132)
1P	50/50	70	0	30	0	0	0	0.124 (0.010)	2.35 (0.13)	0.155 (0.018)
1Q	50/50	60	10	30	0	0	0	0.230 (0.037)	5.48 (0.70)	0.652 (0.158)
1R	25/75	70	0	30	0	0	0	0.131 (0.007)	2.20 (0.15)	0.148 (0.019)
1S	25/75	60	10	30	0	0	0	0.196 (0.017)	4.40 (0.52)	0.459 (0.101)
1T	25/75	67	0	30	0	3	0	0.134 (0.013)	2.18 (0.15)	0.150 (0.020)
1U	25/75	57	10	30	0	3	0	0.220 (0.022)	4.20 (0.60)	0.462 (0.121)
1V	25/75	60	0	30	0	0	10	0.222 (0.049)	4.67 (0.80)	0.499 (0.196)
1W	0/100	70	0	30	0	0	0	0.127 (0.008)	2.26 (0.15)	0.154 (0.021)
1X	0/100	67	0	30	0	3	0	0.145 (0.022)	2.15 (0.30)	0.159 (0.044)

[a] Numbers in parentheses are one standard deviation.

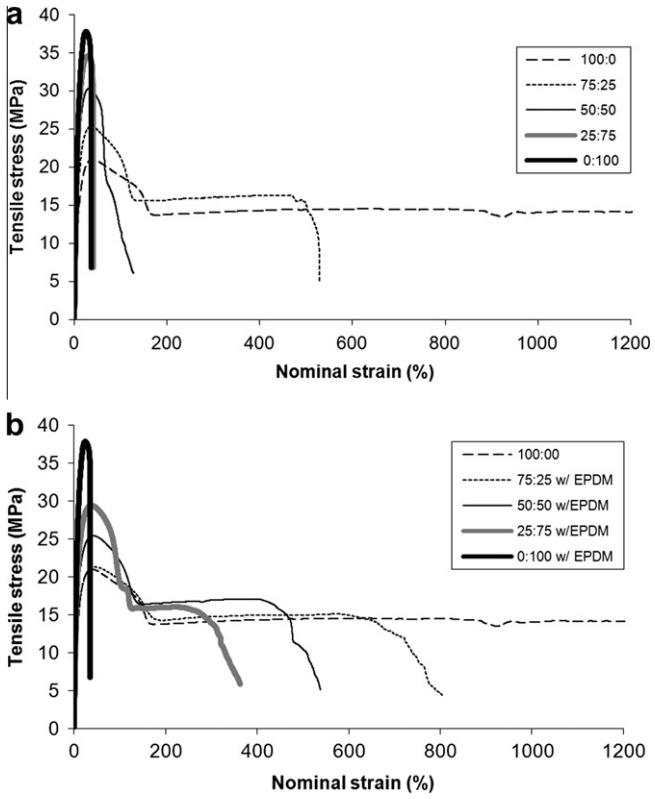

Fig. 2. Tensile curves for unfilled plastics and their blends without (a) and with (b) elastomer. Ratios in legend are HDPE:PP weight ratios.

The compounded pellets were subsequently dried at 105 °C and then injection molded using a 32 ton reciprocating screw injection molder (Sentry VS, Cincinatti Milacron) into tensile, flexural, Izod impact, and drop weight impact specimens.

2.4. Characterization

Tensile [36], flexural [37], and Izod impact [38] properties were evaluated according to the appropriate ASTM standards. For tensile tests, type I specimens were tested at a strain rate of 1 mm/mm min. The initial slopes of the tensile and flexural curves were determined by fitting a hyperbolic tangent function to the initial curve portion from the origin to yield point. All correlation coefficients were 0.995 or greater. High speed puncture impact tests were performed on disk shaped specimens that were 2 mm thick and 80 mm in diameter according to ASTM D3793 [39]. An impactor speed of 1 m/s second was used for the tests. A minimum of five replicates were tested for all procedures. Tukey's multiple comparisons tests were used to determine whether properties of different formulations were significantly different at a 95% confidence level [40].

Fracture surfaces of notched impact specimens were coated in a gold–palladium alloy and examined using a using a Zeiss EVO40 scanning electron microscope (Carl Zeiss SMT, Inc., Thornwood, New York) to investigate morphology and adhesion of blend components.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Unfilled HDPE, PP, and their blends

The mechanical properties of the unfilled blends and composites are summarized in Tables 1–3. The initial HDPE and PP plastics exhibited very different mechanical performance, with the PP having much larger moduli and strengths but also lower impact performance and strains at yielding and failure (Table 1). The tensile moduli of the blends without EPDM are clearly proportional to the relative amounts of HDPE and PP in the blends. Not surprisingly, adding 10% of the low modulus EPDM reduces the moduli of the blends. The reductions in moduli were about 25% in tensile tests and about 20% in flexural tests. This is a common limitation of using elastomers as compatibilizers in plastic blends. However, all moduli for the blends were at least that of the unblended HDPE. Tensile yield stresses and strains also appear to follow a simple rule of mixtures. Adding 10% EPDM allows the blends to yield more easily, at about 16% lower stress, but at about 35–40% higher strain. The largest yield strains found were for the blends with 25:75 and 50:50 HDPE:PP blend ratios containing EPDM, and exceeded those of the unblended plastics.

Representative tensile curves for the unfilled blends are shown in Fig. 2. The large strains exceeded the range of our strain gauge and the strains shown are nominal strains based on the separation of the specimen grips. Tests on unfilled HDPE were stopped after 1200% nominal strain. Unlike moduli and yield properties, additions of even 25% PP to HDPE greatly reduced nominal strains at failure. This negative deviation from a rule of mixtures demonstrates the embrittlement common in incompatible plastic blends.

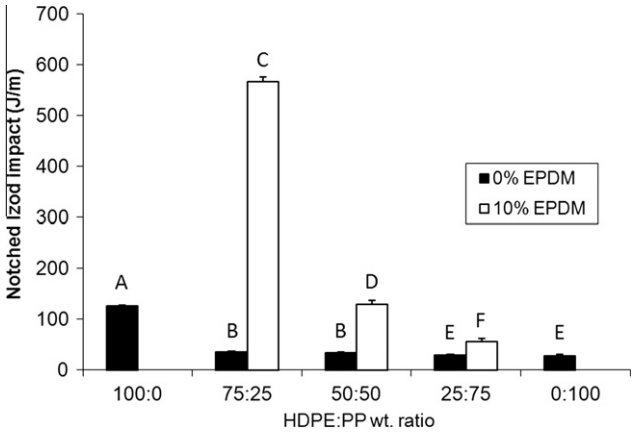

Fig. 3. Effect of elastomer on notched impact tests of unfilled plastics and their blends. Bars with the same letter are not significantly different at a 95% confidence.

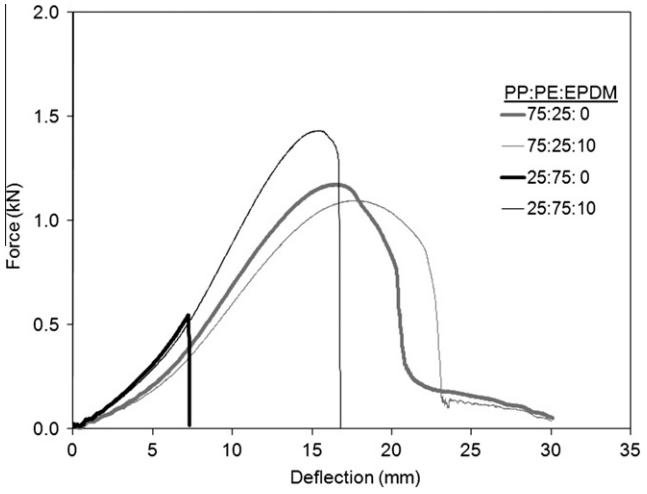

Fig. 4. Effect of EPDM elastomer on high speed puncture tests for several HDPE/PP blends.

Adding EPDM to the blends greatly improved the nominal strains at failure, especially those with the low PP content.

Improving impact performance is one of the major reasons for adding elastomers to polymers. For reversed notch impact tests, only the unfilled PP and the 25:75 HDPE:PP without EPDM were broken during testing. As with the nominal strain at failure in the tensile tests, notched impact energy was greatly reduced with addition of as little as 25% PP to HDPE if no EPDM was added. However, the addition of EPDM greatly improved the situation. While adding 25% PP reduced the notched impact energy of HDPE by over 70%, adding EPDM to the 75:25 HDPE:PP blend increased its notched impact energy over 15-fold (Fig. 3). This blend also exhibited considerable stress whitening due to microvoids. This improvement fell off quickly as the PP content was increased, but still resulted in notched impact energies well above the blends without EPDM.

For high speed puncture tests, addition of EPDM improved impact performance only in the brittle, PP-rich blends (Table 2). Adding EPDM to the PP-rich blends led to a change from brittle to ductile behavior (Fig. 4) resulting in large improvements in the measured parameters (Table 2). However, the PE-rich blends already exhibited ductile behavior and adding EPDM did little to improve the high speed puncture test results.

Selected HDPE:PP blends were investigated as matrices in wood–plastic composites. The formulations investigated are summarized in Table 1. The HDPE, PP and elastomeric compatibilizers (when used) were fed into the main feed throat and the blend formed in the first part of the extruder (Fig. 1). The wood flour was added further down the extruder and compounded with the polymer blend along with any coupling agents used to improve adhesion between the wood flour and polymer blend. The coupling agent used was either a maleated PE (MAPE) for HDPE-rich blends or maleated PP (MAPP) for PP-rich blends. These maleated polyolefins are commonly used to improve the adhesion between wood and polyolefins. The anhydride moiety can react with the hydroxyls on the wood surface and form ester bonds and the polyolefin backbone can incorporate itself into the bulk polymer. In addition to the EPDM, a maleated EPDM was also investigated since it has the potential to interact with both the plastics and the wood flour.

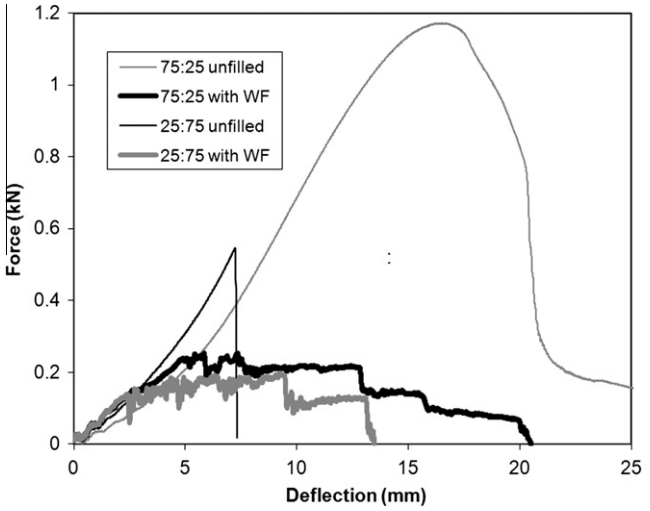

Fig. 6. High speed puncture tests on selected blends and composites without additives. Ratios shown are PE:PP weight ratios. WF is wood flour.

3.1.2. Composites without additives

Adding 30% wood flour to the blend without elastomer or coupling agent yielded expected large increases in moduli and large reductions in reverse-notched Izod impact performance. These are the usual trade-offs in mechanical performance when wood flour is added to HDPE or PP. The wood flour has a much higher modulus than either plastic and improves the composite moduli accordingly. However, the wood flour particles act as stress concentrators, making crack initiation easier especially at high defor-

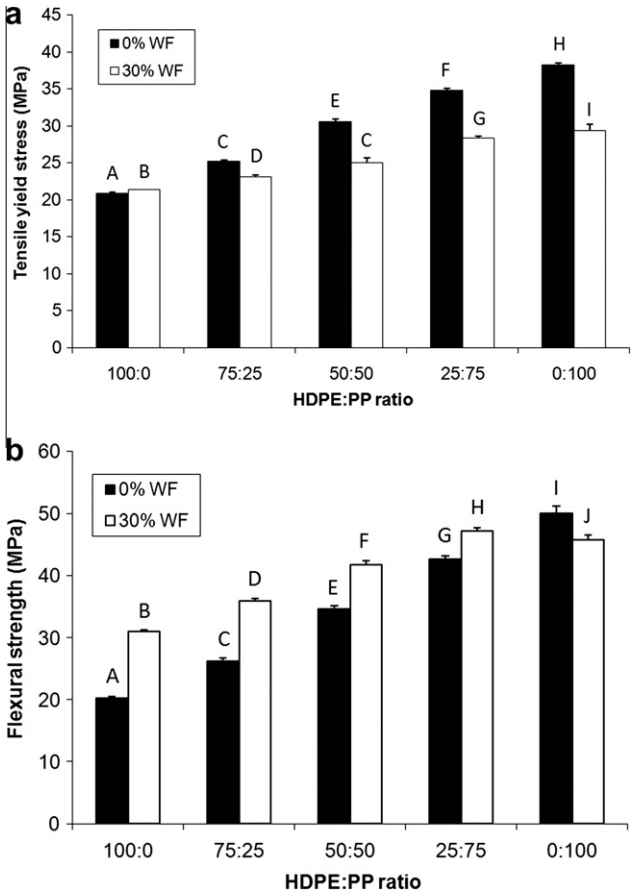

Fig. 5. The effect of WF on the yield stress and flexural strength of plastic blends. Bars with the same letter are not significantly different at a 95% confidence.

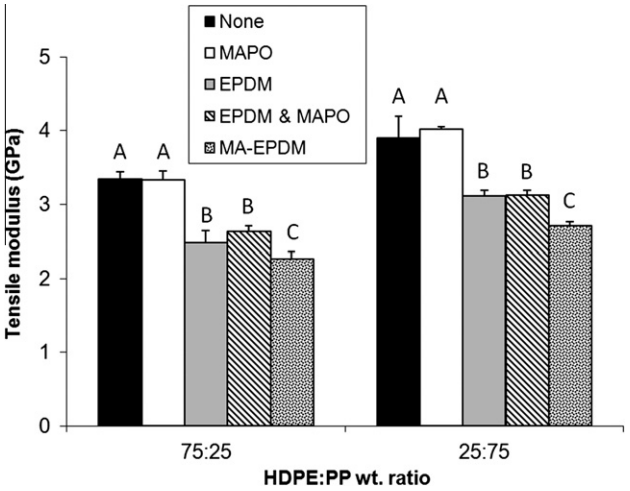

Fig. 7. Effect of several additives on the tensile moduli several blends filled with 30% wood flour. Maleated polyolefin (MAPO) refers to MAPE for the 75:25 HDPE:PP blend and MAPP for the 25:75 HDPE:PP blend. Bars with the same letter for set of composites are not significantly different at a 95% confidence.

mation rates as in the reverse-notched impact tests. With the exception of the unfilled HDPE, notched Izod impact energy did not change much when 30% wood flour was added to the plastics and their blends in the absence of elastomer or coupling agent since the values were already very low. However, adding 30% wood flour to the tough unblended HDPE matrix greatly reduced the notched Izod impact energy.

Interestingly, the tensile yield strengths were reduced but the flexural strengths were increased with addition of wood flour (Fig. 5). One possible explanation for the difference between the strength properties may have to do with orientation of the wood particles. In injection molded composites, particles can orient parallel to the mold filling direction at the surface and transverse to it in the core layer [41]. Therefore, reinforcement is more likely in the surface layer, where the wood flour particles would be more favorably oriented. However, this reinforcement would not be expected to be large since the wood flour has a low aspect ratio and good adhesion between the wood and plastics would not be expected. Since failure usually occurs on the tension surface during flexural testing (whereas tensile strength is more of a bulk property), this limited reinforcement might increase flexural strength due to parallel orientation of the wood flour at the surface but reduce tensile strength if the overall wood flour orientation is transverse to the mold filling direction. However, injection molded composite morphology is complex and more research would be necessary to adequately explain this behavior. For both flexural and tensile tests, the relative strength of composites decreased with increasing PP content. This might be due to better mechanical interlocking of the wood flour with HDPE because of lower melt viscosity. This would result in better wood–plastic stress transfer and higher strengths.

Fig. 6 shows load versus defection for the high speed puncture tests of several of the PP–HDPE blends and their composites without additives. The unfilled HDPE-rich and PP-rich blends showed ductile and brittle behavior, respectively. Both of the composites fractured at much lower applied loads than the unfilled blends and much of their energy absorption was due to tearing and damage accumulation once damage was initiated. This point is characterized by discontinuities in the curves at about 5 and 2.5 mm of deflection for the HDPE-rich and PP-rich composites, respectively. This incipient damage point can be very important depending on application. While continued damage accumulation can add a measure of safety by dissipating energy and avoiding catastrophic failure in some applications, the incipient damage point may be

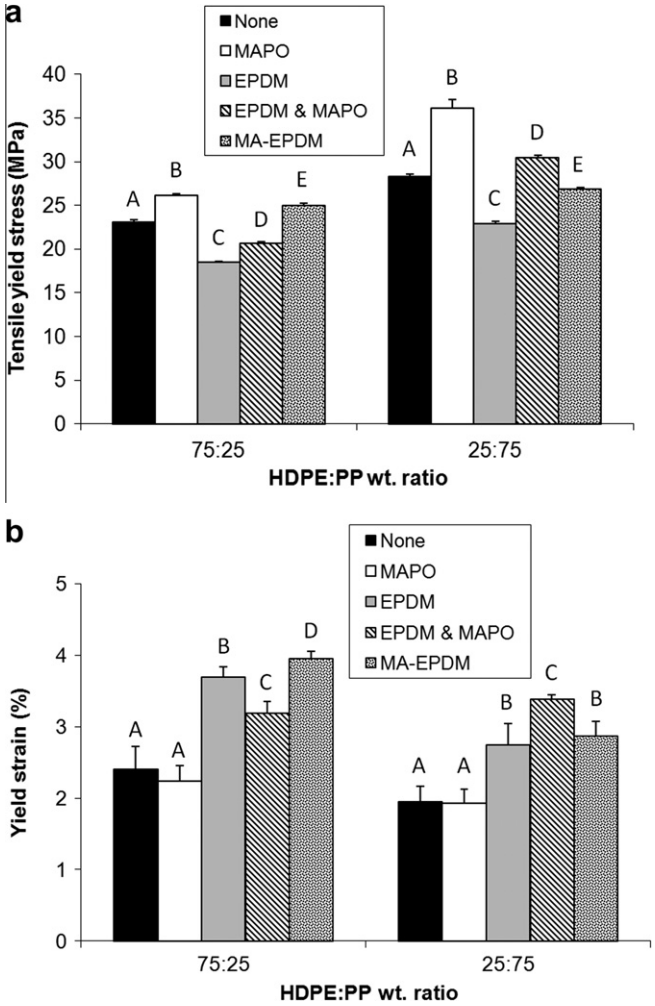

Fig. 8. Effect of several additives on the tensile yield stress (a) and strain (b) for several blends filled with 30% wood flour. Maleated polyolefin (MAPO) refers to MAPE for the 75:25 HDPE:PP blend and MAPP for the 25:75 HDPE:PP blend. Bars with the same letter for each set of composites are not significantly different at a 95% confidence.

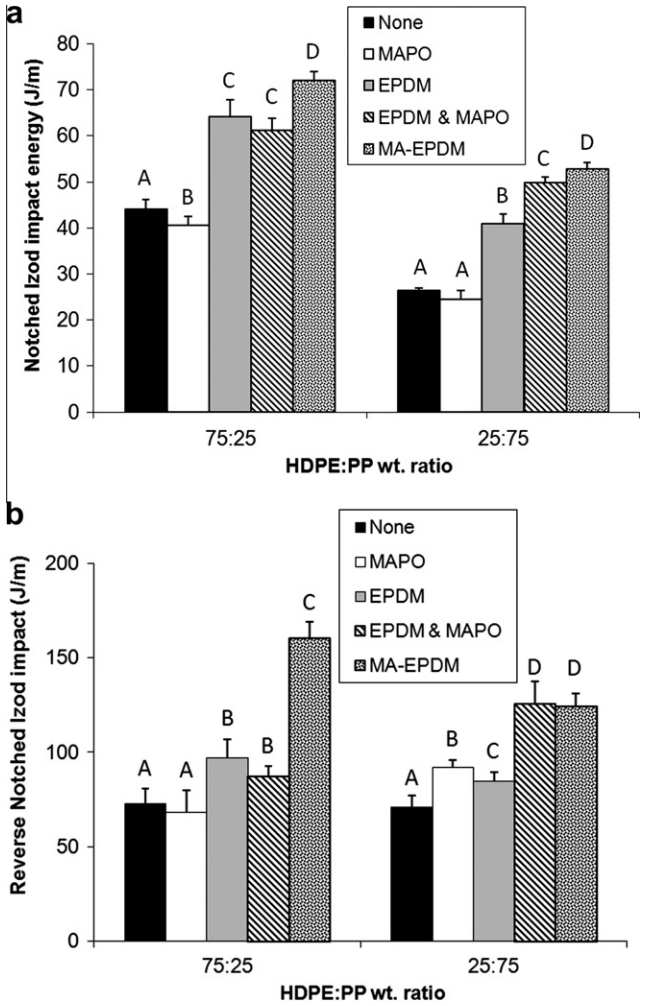

Fig. 9. Effect of several additives on notched (a) and reverse-notched (b) Izod impact energies for several blends filled with 30% wood flour. Maleated polyolefin (MAPO) refers to MAPE for the 75:25 HDPE:PP blend and MAPP for the 25:75 HDPE:PP blend. Bars with the same letter for each set of composites are not significantly different at a 95% confidence.

considered failure in others. Table 3 summarizes the results at the incipient damage point for all composites.

3.1.3. Composites with additives

Figs. 7–9 show the effects of the different additives and HDPE:PP ratio on selected properties. In these figures, MAPO refers to maleated polyolefins: MAPE in HDPE-rich composites or MAPP in PP-rich composites. Adding MAPO to the composites had little influence on modulus (Fig. 7). Not surprisingly, adding elastomers with lower modulus reduced the moduli of the composites but they were still well above those of the unfilled blends.

Generally, adding maleated polyolefins (MAPO) increased the yield properties of the composites (Fig. 8) but the increases were greater in the composites made with the 25:75 HDPE:PP blend, suggesting that the MAPP was a more effective coupling agent than the MAPE in their respective composites. Adding EPDM decreased the yield stress but increased the yield strain in the HDPE-rich composites. Adding both the MAPO and EPDM tended to give performance in between that of the MAPO or EPDM alone. The exception was the yield strain of the 25:75 HDPE:PP blend where, surprisingly, the combination of MAPO and EPDM resulted in larger yield strains than either alone. The MA–EPDM outperformed the MAPO/EPDM combination in the HDPE-rich composites but performed worse in the PP-rich blends.

The MAPOs did little to improve the Izod impact performance except for the reverse-notched energy for the 25:75 HDPE:PP blend. All elastomers or elastomer/MAPO blends improved Izod impact performance. The notched and reversed notched impact energies were increased from about 40–100% and 20–120%, respectively, depending on the elastomer and HDPE:PP ratio. The greatest improvements were with the MA–EPDM for the 75:25 HDPE:PP composites and the MA–EPDM and EPDM/MAPO both gave large improvements in the 25:75 PP:HDPE composites.

In the high speed puncture tests, adding elastomers increased the force and energy required to initiate damage in the composites (Table 3). The greatest increases were found when MA–EPDM was added to PP-rich composite blend resulting in a composite that required about 70% more force and three times the energy to initiate damage. However, these values were still lower than all of the unfilled polymer blends. Somewhat surprisingly, the coupling agents did little to improve the force required to initiate damage in the composites in the high speed puncture tests suggesting that a more flexible interphase is more desirable in preventing damage in the high speed tests.

In summary, the mechanical properties of the plastic blends followed a rule of mixtures with respect to tensile and flexural properties but adding even small amounts of PP to HDPE greatly reduced Izod impact performance. Adding EPDM to the blends reduced moduli and strengths but improved elongational properties (e.g., yield strain, strain at break) and improved impact performance, especially notched impact energies in blends with small to moderate amounts of PP and in high speed puncture properties of PP-rich blends. Adding 30% wood flour to the blends greatly increased moduli and yielded more favorable strength properties in PE-rich blends than in PP-rich blends. However, Izod impact behavior was generally greatly reduced. High speed puncture test showed early initiation of damage and that much of the energy absorbed was due to accumulation of damage. Adding MAPOs to the composites tended to improve the strength properties of the

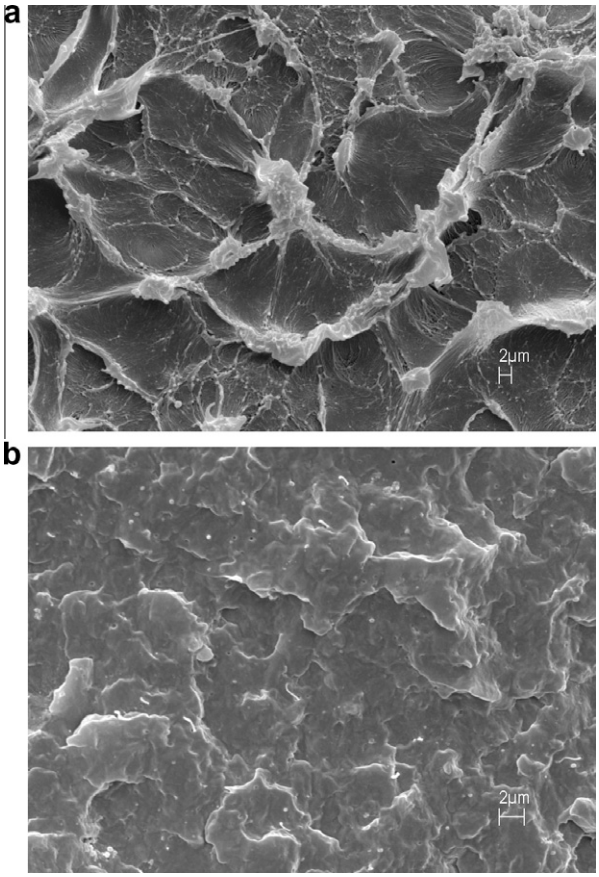

Fig. 10. Fracture surfaces of notched Izod impact specimens of HDPE (a) and PP (b). Micrographs taken near fracture initiation site near the notch.

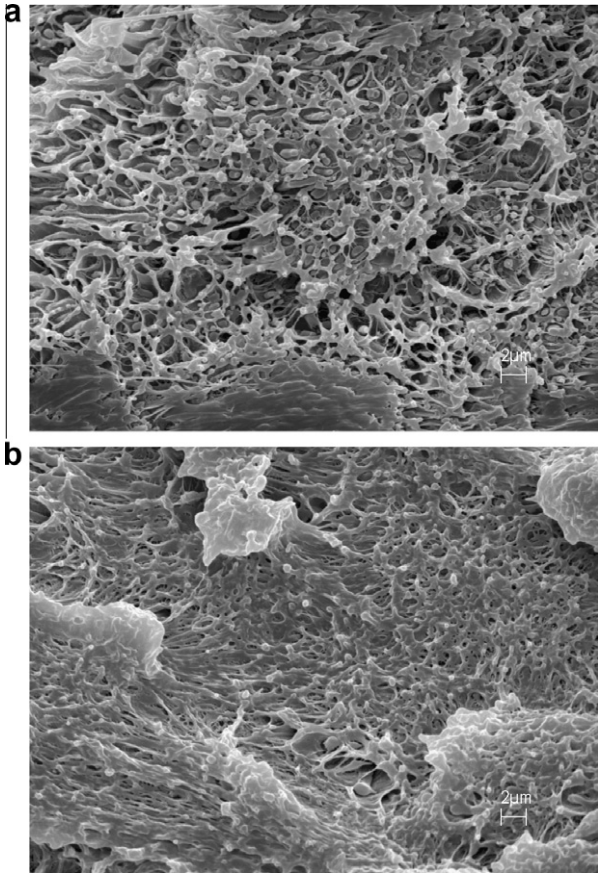

Fig. 11. Fracture surfaces of notched impact specimens: 75:25 HDPE:PP blend without (a) and with (b) EPDM.

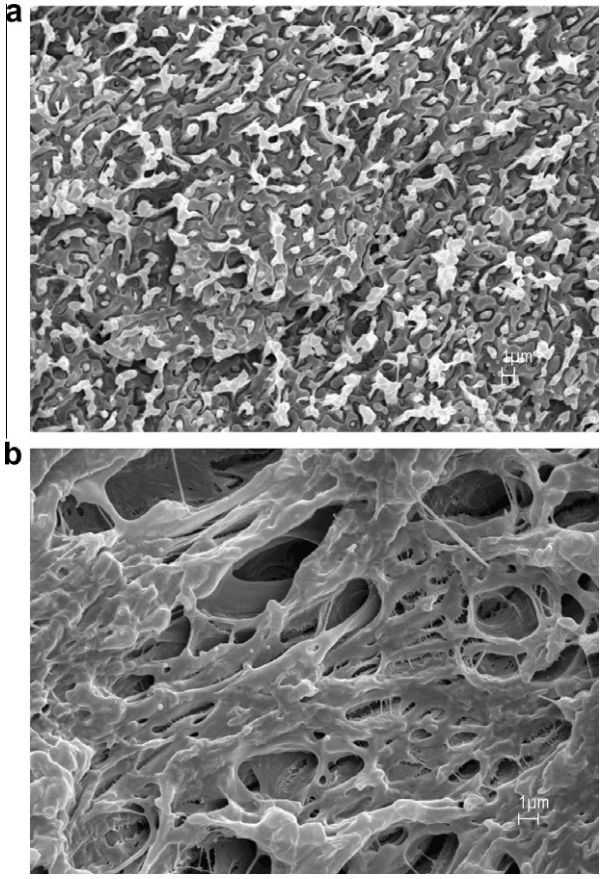

Fig. 12. Fracture surfaces of notched impact specimens of 50:50 HDPE:PP blend without (a) and with (b) EPDM.

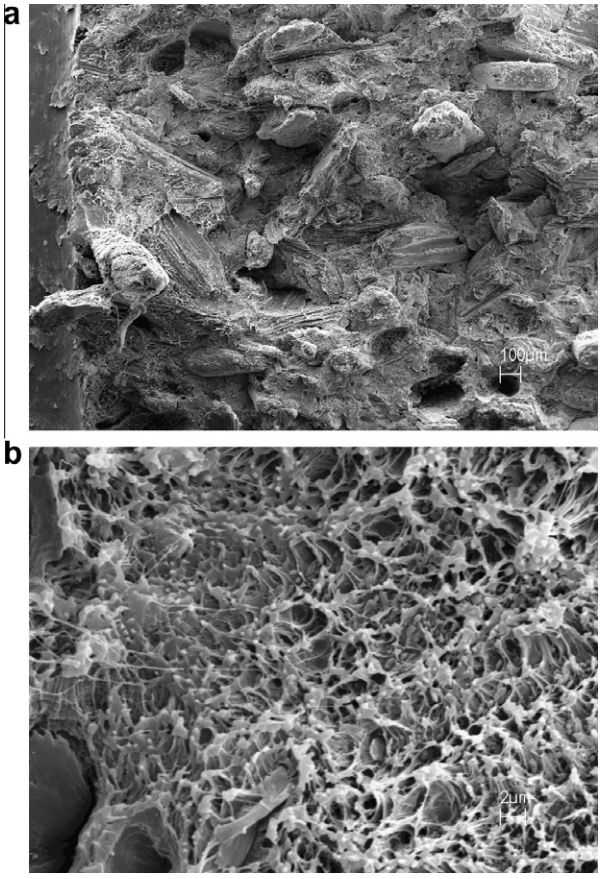

Fig. 13. Fracture surfaces of notched impact specimen of 75:25 HDPE:PP blend containing 30% wood flour at different magnifications.

composites, although this improvement was likely limited by the low aspect ratio of the wood flour. MAPP appeared more effective in PP-rich blends than MAPE did in HDPE-rich blends. Adding elastomers to the composites also reduced moduli and strength properties but improved the Izod impact properties to various extents based on elastomer type, HDPE:PP ratio, and whether it was used in combination with a MAPO. In high speed puncture tests, adding elastomers, especially MA–EPDM increased the force and energy required to initiate damage in the composites.

3.2. Microscopy

The fracture surfaces of the notched impact specimens were investigated using scanning electron microscopy (SEM). Figs. 10–14 are micrographs of fracture surfaces near the notch and in the center of the specimens where the material is most constrained and where the fracture usually initiates. Micrographs in the figures are of representative areas or areas with significant features. However, there can be considerable variability from region to region in a particular sample. Summarized findings are a result of a general survey of the samples and caution should be exercised in drawing broad conclusions from a specific SEM micrograph.

Fig. 10 shows fracture surfaces of the unblended plastics. Microductile behavior can clearly be seen for HDPE but the PP micrograph shows brittle fracture. This is reflected in the impact energies of the plastics.

Fig. 11 shows the HDPE-rich blend both with and without EPDM at the same magnification. There is considerable micrometer-scale deformation (i.e. microductility) of the HDPE matrix in both Figs. 11a and b. However, when the entire fracture surfaces were examined, the regions of high microductility were more widespread in the blend with EPDM. In Fig. 11a, distinct domains of PP can be seen in a continuous HDPE phase. The cavities surrounding the PP domains suggest that the two phases were easily separated when the blend was deformed. In contrast, the PP domains are more difficult to distinguish and appear smaller in Fig. 11b than in Fig. 11a suggesting improved compatibility between the HDPE and PP, which often leads to better impact performance [28]. Domain size is determined by a number of factors including the viscosity ratio of the polymers being blended, the shearing during processing, and the molecular architecture [4]. As a result the morphology can depend heavily on the processing parameters. For example, changing the temperature profile during compounding can change the relative viscosity ratio and, therefore, the domain size and mechanical performance. An advantage of adding compatibilizers is that they tend to stabilize morphology and reduce the variability of the blend morphology [4].

The PP-rich blend without EPDM showed little microductility, suggesting brittle failure. Also, gaps at phase interfaces were found suggesting poor adhesion between HDPE and PP. Since EPDM has both PE and PP components, its solubility parameter is between that of PP and HDPE and EPDM migrates to the PP–HDPE interfaces [35]. It is harder to distinguish the HDPE–PP interfaces in the blend with EPDM and fewer gaps at the interfaces are noticeable.

The 50:50 HDPE:PP blend showed a co-continuous morphology (Fig. 12). The more ductile HDPE can clearly be distinguished from the PP in the blend without EPDM. In the blend with EPDM, domains were less distinguishable and the yielding was less localized (Fig. 12b). Since yielding is an energy intensive process, it is not

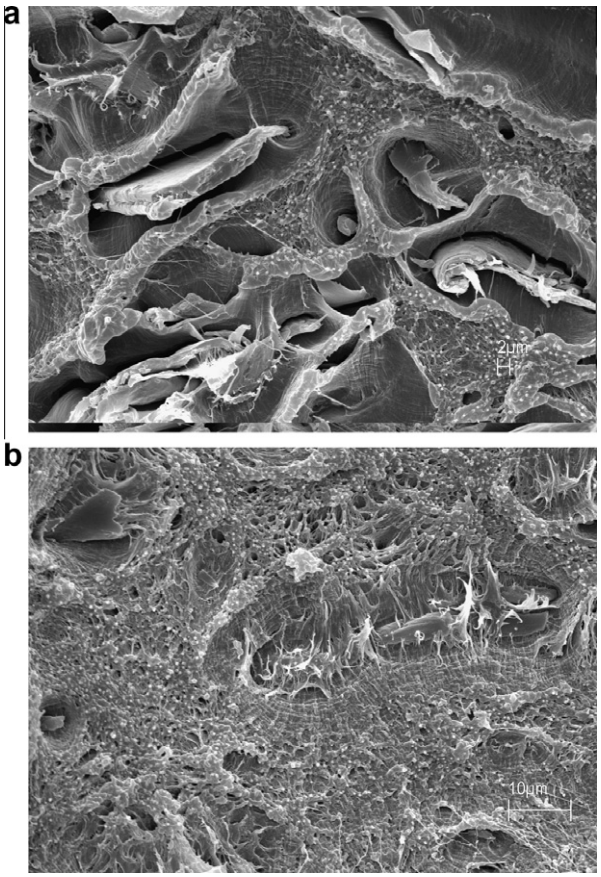

Fig. 14. Fracture surfaces of notched impact specimens of 75:25 HDPE:PP with 30% wood flour and EPDM (a) or MA–EPDM (b).

surprising that the impact energies were greatly increased when EPDM was added.

Fig. 13 shows micrographs of the 75:25 HDPE:PP blend with 30% WF at very different magnifications. Because of the very different sizes of the wood flour particles and plastic domain sizes, it is somewhat difficult to show the interaction between the various components in a single image. However, the resin-rich area shown in the Fig. 13b appears very similar to that of the unfilled blend Fig. 11. The influence of elastomer became more apparent in areas containing fine wood flour particles (Fig. 14). In composites with EPDM, little adhesion was apparent between the matrix and wood flour particles and plastic deformation appeared to initiate from the interfaces between them (Fig. 14a). However, in composites containing MA–EPDM, evidence of better bonding was found (Fig. 14b).

4. Conclusions

The unblended HDPE and PP plastics exhibited very different mechanical performance, with the PP having much larger moduli and strengths but also lower impact performance and elongational properties (strains at yielding and failure).

Blending of the plastics resulted in either small domains of the minor phase in a matrix of major phase or a co-continuous morphology if equal amounts of HDPE and PP were added. The tensile moduli and yield properties of the blends without EPDM were clearly proportional to the relative amounts of HDPE and PP in the blends. However, the nominal strain at break and the notched Izod impact energies of HDPE were greatly reduced by adding as little as 25% of the PP. Adding EPDM to the blends, reduced moduli and strength but increased elongational properties and impact energies, especially in HDPE-rich blends.

Adding wood flour to the blends stiffened but embrittled them, especially the tougher, HDPE-rich blends, though the reductions in performance could be offset somewhat by adding elastomers and coupling agents or a combination of both. Additives need to be tailored to a specific recycled blend. Trade-offs in performance (such as modulus reduction when elastomers are added) need be accommodated and economics considered.

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