

# Rice Straw Fiber Reinforced High Density Polyethylene Composite: Effect of Coupled Compatibilizing and Toughening Treatment

Fei Yao,<sup>1</sup> Qinglin Wu,<sup>1</sup> Hongzhi Liu,<sup>1</sup> Yong Lei,<sup>1</sup> Dingguo Zhou<sup>2</sup>

<sup>1</sup>School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, Louisiana 70803

<sup>2</sup>College of Wood Science and Technology, Nanjing Forestry University, Nanjing 210037, China

Received 28 January 2009; accepted 11 January 2010

DOI 10.1002/app.32946

Published online 27 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** In this study, rice-straw (RS) filled high density polyethylene (HDPE) composites were manufactured by extrusion and injection molding. Three compatibilizers, which are unfunctionalized ethylene/propylene copolymer (uEPR), maleic anhydride grafted EPR (EPR-g-MA) and PE-g-MA, and their combinations were introduced to strengthen fiber-matrix interphase. The mechanical and morphological properties of composites were investigated. For single-compatibilizer system, PE-g-MA or EPR-g-MA alone enhanced tensile, flexural, and impact strengths of resultant composites compared with HDPE/RS system without compatibilizers. Different toughening origins of individual compatibilizer were dis-

cussed based on composites' interphase morphologies and mechanical properties. For combined-compatibilizers system, the PE-g-MA/EPR weight ratio is important for several properties of composites. The optimum ratio was considered as 2 : 1 and 1 : 1 for PE-g-MA/uEPR and PE-g-MA/EPR-g-MA modified composites, respectively. Also, composites modified by combined PE-g-MA/EPR-g-MA showed better impact strength than that modified by PE-g-MA alone. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2214–2222, 2011

**Key words:** compatibilization; mechanical properties; morphology; interfaces

## INTRODUCTION

The use of compatibilizers in natural fiber reinforced polymer composites (NFPC) is to improve poor interphase between hydrophilic fiber and hydrophobic polyolefin matrix. Among numerous compatibilizers, maleic anhydride grafted polyethylene and polypropylene (PE-g-MA and PP-g-MA) are considered to be some of the most effective interphase modifiers for polyolefin-wood/natural fiber composite due to the polar interaction and covalently link between anhydride carbonyl and hydroxyl groups of the fiber surfaces,<sup>1–4</sup> as well as their good compatibility with matrix.<sup>5–9</sup>

Various polyolefinic elastomers, including styrene/ethylene-butylenes/styrene triblock copolymer (SEBS)<sup>5,7,10–12</sup> and ethylene/propylene/diene terpolymer (EPDM),<sup>13,14</sup> have also been of interest because of enhanced performance on impact strength of pure

high density polyethylene (HDPE) and PP matrix. However, the addition of elastomers alone fails to effectively improve the strength and modulus of final composites. Their use even weakens composite strength and modulus properties, although the impact toughness is more or less improved depending on the nature and content of elastomers used. To optimize the balance between stiffness/strength and toughness of NFPC, combination of elastomers with maleated polyolefins as combined modifiers has been reported.<sup>14–16</sup> For instance, Oksman and Clemens<sup>14</sup> studied mechanical properties and morphology of impact modified PP/wood-flour composites, and observed that adding combined 10 phr (per hundred resin) SEBS-g-MA and 2 phr PP-g-MA into the system exhibited more superior impact strength improvement than adding either 10 phr SEBS-g-MA or 2 phr PE-g-MA individually. The tensile strength of system was less decreased even by the incorporation of 10 phr SEBS-g-MA. However, the same improvement was not observed in the EPDM/PP-g-MA or EPDM-g-MA/PP-g-MA modified system. Sumbatsompop et al.<sup>16</sup> investigated the effect of combining both PP-g-MA and other impact modifiers into PP/wood-sawdust system, and suggested that 2.0 wt % PP-g-MA concentration into the composites containing 11.1 wt % total impact modifier could optimize overall mechanical properties.

Correspondence to: Q. Wu (wuqing@lsu.edu).

Contract grant sponsor: USDA Rural Development Biomass Initiative Program; contract grant number: 68-3A75-6-508.

Contract grant sponsor: Louisiana Board of Regents Industrial Tie Subprogram; contract grant number: LEQSF:2005-08-RD-B-01.

**TABLE I**  
**Characteristics of Polymeric Resins Used in this Study**

Polymer	Commercial designation	Property	Manufacturer
HDPE	HD6706.17	MFR (190°C/2.16 kg) = 6.1 g/10 min, density = 0.952 g/cm <sup>3</sup>	ExxonMobil Chemical (Houston, TX)
PE-g-MA	Epolene™ G2608	MFR (190°C/2.16 kg) = 6–10 g/10 min, $M_w$ = 65,000g/mol, acid number = 8 mgKOH/g	Eastman Chemical (Kingsport, TN)
uEPR	Vistalon™ 722	MFR = 1 g/10 min (manufacturer method), 72% ethylene	ExxonMobil Chemical (Houston, TX)
EPR-g-MA	Exxelor™ VA1801	MFR (230°C/10 Kg) = 9 g/10 min, density = 0.87 g/cm <sup>3</sup> , ethylene: propylene: MA = 43 : 53 : 1.21	ExxonMobil Chemical (Houston, TX)

Although some work has been done, there is a lack of understanding on how the ratio of the combined modifiers affects various mechanical properties of the resultant composites.

Ethylene/propylene copolymer (EPR) is one of the polyolefin-based thermoplastic elastomers. It offers excellent thermal/oxidative stability and weatherability compared with conventional EPDM due to its fully saturated backbone. MA functionalized EPR (EPR-g-MA) could further increase both filler-matrix adhesion and impact strength by promoting the favorable core-shell encapsulation.<sup>17,18</sup> Moreover, EPR copolymers are generally classified into semicrystalline and amorphous ones depending on stereoregularity and composition of the monomer sequence. The former is considered somewhat better for improving various properties of matrix than the latter in some research.<sup>19</sup>

Some work has been done in rice-straw (RS)/polymer composites.<sup>20–22</sup> However, RS has not been widely used as reinforced filler for polymer system compared to wood. Moreover, there is a lack of detailed investigation on the effect of various compatibilizers on HDPE/RS system at this point. The objective of the study described in this article was to investigate the influence of various compatibilizers, including PE-g-MA, EPRs, and their combinations on mechanical and thermal properties, as well as morphologies of the rice straw reinforced HDPE composites.

## EXPERIMENTAL

### Material and experimental design

Rice straw (RS) was obtained from Louisiana State University (LSU) Ag Center's Crowley Rice Research Station in Crowley, Louisiana, with particle size between 20 and 28 meshes (900–1200 μm). Related information of the polymer and various compatibilizers used in the study is listed in Table I.

Experiment design included two factorial experiments. The first experiment was to investigate the effect of individual compatibilizer, consisting of nine blends covering three compatibilizers (PE-g-MA, uEPR, and EPR-g-MA)

and three loading rates (1.5, 2.9, and 4.3 wt % of total composite weight). The second experiment was designed to study the effect of combined compatibilizers, consisting of twelve blends covering two combined compatibilizer systems (PE-g-MA/uEPR and PE-g-MA/EPR-g-MA), two compatibilizer contents (1.5 and 4.3%), and three PE-g-MA/EPR ratios (2 : 1, 1 : 1, and 1 : 2).

### Sample preparation

Rice straw fiber was oven-dried at 80°C for 12 h before compounding. Melt compounding was performed using an intermesh, counter-rotating Brabender twin-screw extruder (Brabender Instruments, Hackensack, NJ) with a screw speed of 40 rpm. All raw materials were feeded into the extruder by two feeders simultaneously and every single sample was prepared separately. The temperature profile of the extruder barrels was 150–175–175–175–175°C from feeder to die. The extrudates were quenched in a cold water bath and then pelletized into granules. After being oven-dried at 100°C for 12 h, the granules were injection-molded into standard mechanical test specimens using a Batenfeld Plus 35 injection molding machine (Batenfeld, NJ). The injection temperatures were 190 and 180°C for HDPE/RS composites and virgin HDPE, respectively. All specimens were then conditioned for 72 h at a temperature of 23°C ± 2°C and a relative humidity of 50% ± 5% for later characterization.

### Characterization

Mechanical properties testing

Tensile and flexural (three-point bending) strength/modulus were measured using an Instron 5582 testing machine (Instron, Norwood, MA) following ASTM D638 and ASTM D790, respectively. Izod impact strength was measured using a Tinius Olsen Mode 1892 impact tester (Tinius Olsen, Horsham, PA) following ASTM D256. Five replicates were carried out for each test and each blend, and corresponding means and standard deviations were reported. Duncan's multiple range tests for pair-wise comparison were carried

**TABLE II**  
**Summary of Mechanical Properties of Virgin HDPE and Resultant HDPE/RS Composites Modified by Individual Compatibilizer**

System <sup>a</sup>	Compatibilizer content (wt %) <sup>b</sup>	Strength property			Modulus property	
		Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (KJ/m <sup>2</sup> )	Tensile modulus (GPa)	Flexural modulus (GPa)
Control group						
Virgin HDPE		18.9 (0.2)G <sup>c,d</sup>	21.3 (0.1)G	8.12 (0.21)A	0.26 (0.02)D	0.80 (0.01)H
HDPE/RS w/o compatibilizer		20.3 (0.4)E	31.7 (0.8)E	3.20 (0.14)FG	3.36 (0.10)B	2.72 (0.06)A
HDPE/RS/PE-g-MA						
	1.5	22.5 (1.2)C	38.8 (0.6)B	4.62 (0.29)C	2.72 (0.26)C	1.78 (0.04)E
	2.9	24.2 (0.5)B	41.7 (0.7)A	4.68 (0.14)C	2.70 (0.39)C	1.87 (0.07)E
	4.3	26.0 (0.5)A	41.3 (0.7)A	5.34 (0.13)B	2.75 (0.25)C	1.68 (0.05)F
HDPE/RS/uEPR						
	1.5	19.3 (0.6)FG	33.0 (0.8)D	3.01 (0.18)G	4.26 (0.35)A	2.59 (0.11)B
	2.9	18.7 (0.3)G	31.5 (0.7)E	3.27 (0.12)F	3.46 (0.15)B	2.54 (0.11)B
	4.3	19.8 (0.6)EF	30.1 (0.9)F	4.74 (0.17)C	2.72 (0.38)C	1.59 (0.07)G
HDPE/RS/EPR-g-MA						
	1.5	22.4 (0.4)C	33.7 (0.5)D	3.60 (0.10)E	3.32 (0.18)B	2.24 (0.02)C
	2.9	21.5 (0.1)D	35.6 (0.3)C	4.31 (0.18)D	3.30 (0.05)B	2.17 (0.07)CD
	4.3	22.9 (0.6)C	38.1 (0.4)B	5.12 (0.32)B	2.92 (0.20)C	2.14 (0.09)D

<sup>a</sup> HDPE/RS = 60 : 40 (wt %) fixed for all composites.

<sup>b</sup> The content of each compatibilizer was based on the total composite weight.

<sup>c</sup> Mean values with the same capital letter for each property are not significantly different at the 5% significance level.

<sup>d</sup> Numbers in the parenthesis are standard deviation based on five specimens.

out to test the effect of various treatments on the composite properties using SAS 9.1 (SAS Institute, NC).

#### Scanning electron microscopy (SEM) analysis

The scanning electron microscope (Hitachi S-3600N VP-SEM, Japan) was employed to analyze the morphology of impact-fractured surfaces of resultant composites. Before observation, the fractured surfaces of the impact specimens were coated with gold to improve the surface conductivity. The acceleration voltage used was 15 KV.

#### Dynamic mechanical analysis (DMA)

Storage modulus  $E'$  and loss modulus  $E''$  of the specimens ( $63.5 \times 12.5 \times 3$  mm) were determined by TA DMA Q800 (TA Instruments, New Castle, DW) using a dual cantilever mode with a span of 35 mm. The measurements were carried out in a temperature range of 25–100°C at a frequency of 1 Hz.

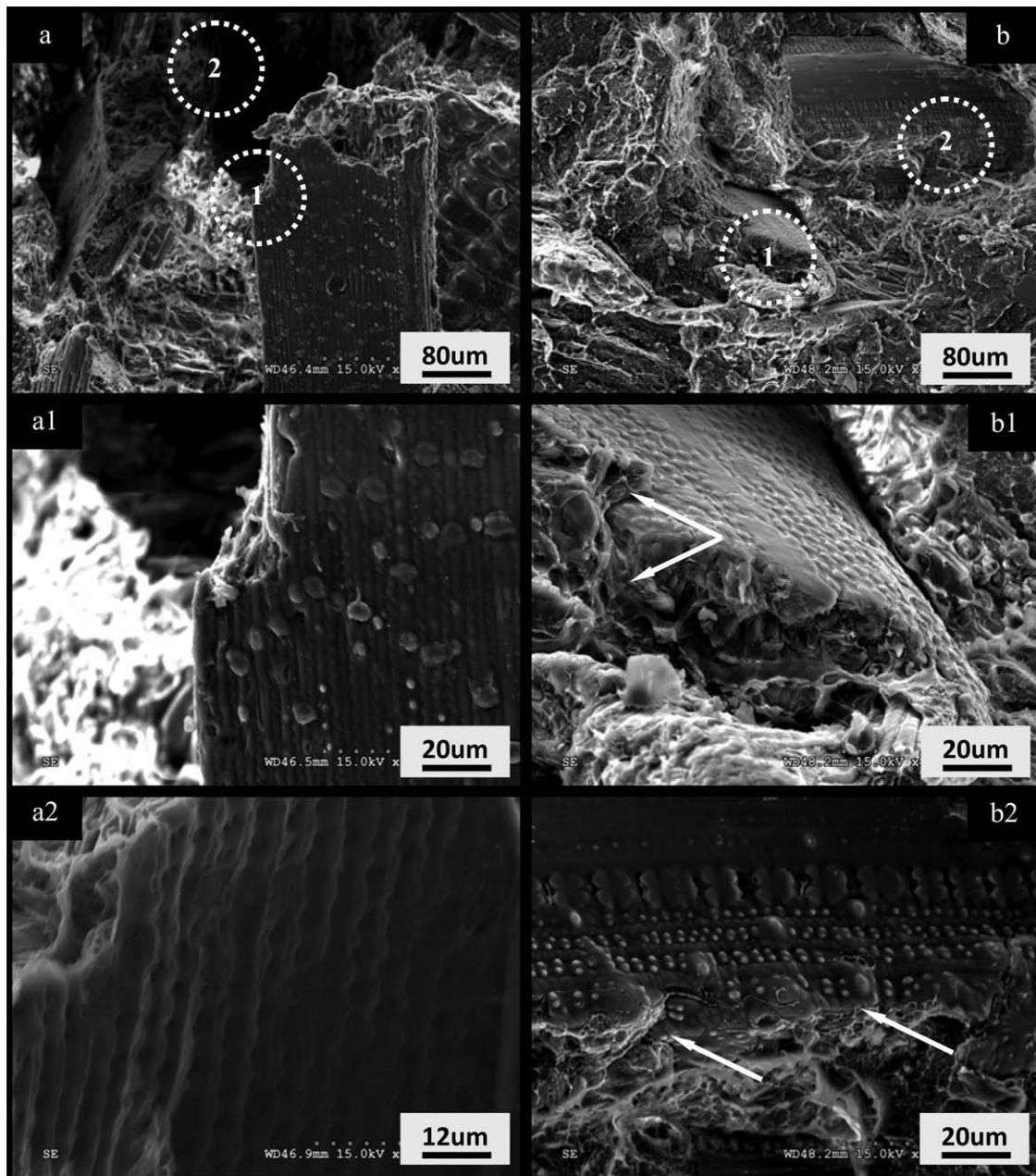
## RESULTS AND DISCUSSION

### Effect of individual compatibilizer type and loading level

Experiment one was designed to investigate the effect of individual compatibilizer and its content on properties of the resultant composites. Their mechanical strength and modulus properties are summarized in Table II along with Duncan's comparison results (the highest to the lowest ranking, A to J) for

each category. The mechanical properties of virgin HDPE and HDPE/RS composite without compatibilizer are also listed as the controls. As expected, unmodified RS/HDPE composite showed better flexural strength than pure HDPE; but its impact strength was significantly lower than the latter due to poor interfacial bonding between matrix and fiber.<sup>14,23</sup> It is also noted that the fibers were randomly-oriented while the degrees of exfoliation of the fiber bundles were considered the same in all composites, due to the same manufacture process. Therefore, mechanical properties' change of various composites was primarily caused by the addition of compatibilizers.

Three compatibilizers showed different influences on the three strength properties of composites. Compared with unmodified binary HDPE/RS composites, the addition of PE-g-MA dramatically improved strength properties of composites (up to 28, 32, and 67% in tensile, flexural and impact strengths, respectively, Table II). The improved tensile strength usually benefits from enhanced adhesion between components or improved matrix-filler interface nature, therefore PE-g-MA promoted interfacial bonding between hydrophilic RS filler and hydrophobic HDPE matrix. The SEM images taken from impact fractured surfaces supported this argument. It showed that, without any compatibilizers [Fig. 1(a)], fiber bundles (circle 1) had fairly smooth surfaces and were devoid of HDPE matrix. Also, typical pulled-out traces (circle 2) are remarkably visible everywhere on the fracture surface. These



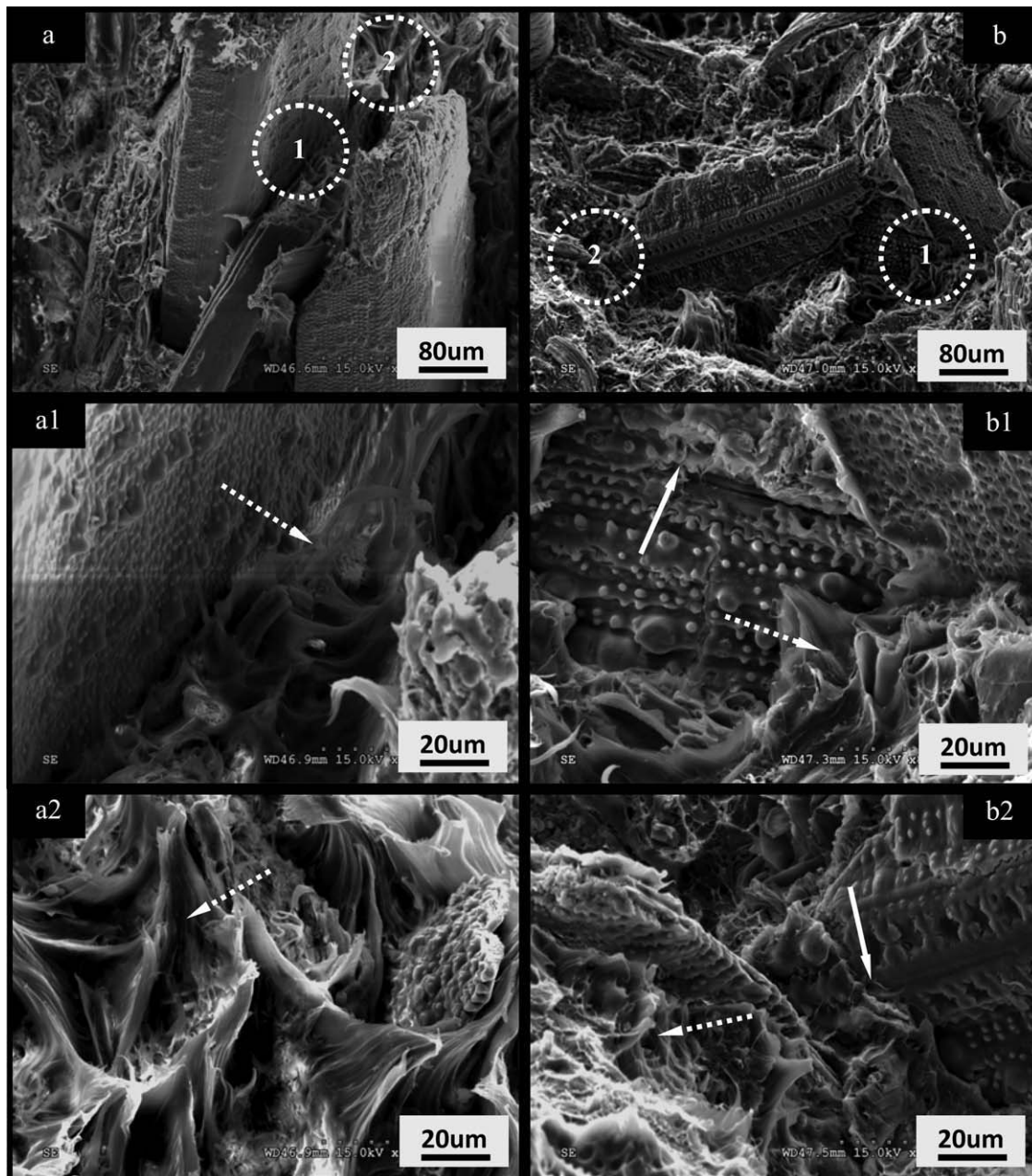
**Figure 1** SEM micrograph of impact-fractured surfaces of composites: (a) without compatibilizer; (b) modified by PE-g-MA. Images a1, a2, and b1, b2 show local details corresponding to Circle 1 and 2 in Image a and b, respectively.

characteristics indicate poor interfacial adhesion between the filler and the matrix. With the addition of 4.3 wt % PE-g-MA [Fig. 1(b)], pulled-out trace is very unusual and the broken fibers are normally embedded in the matrix without evident gap in the interfacial area (circles 1 and 2) evidencing good interface bonding (solid arrows). In addition, plastic deformation of the surrounding matrix involved is not obvious, which suggests that the fracture of RS itself instead of debonding is the main energy dissipation mode in this case.

The addition of uEPR failed to provide positive effects on tensile and bending strengths of composites. Specifically, tensile strength of HDPE/RS/

uEPR composites was even lower than that of the control composite significantly, suggesting possible worse matrix-RS interphase. The addition of uEPR generated a very coarse fracture surface [Fig. 2(a)], which is fairly similar to that in the unmodified system [Fig. 1(a)], indicating a weak bonding between HDPE and filler. However, the signs for plastic deformation (dashed arrows) of local matrix (circles 1 and 2) appeared more evident than unmodified one, indicating the toughening of matrix.

EPR-g-MA showed moderate improvement effects on the three strength properties of composite (Table II), where tensile and impact strengths increased 6–13 and 13–60%, respectively, with respect to the control

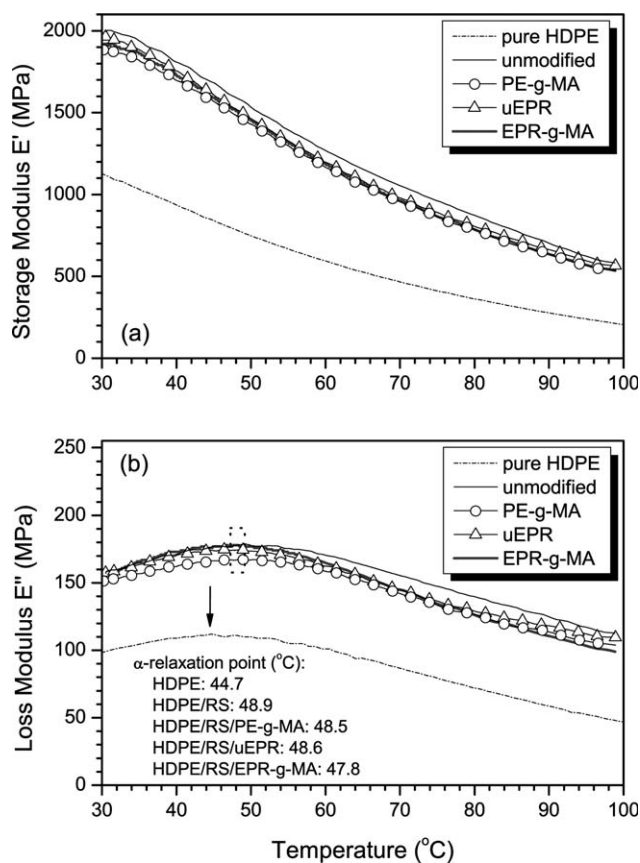


**Figure 2** SEM micrograph of impact-fractured surfaces of composites: (a) modified by uEPR and (b) modified by EPR-g-MA. Images a1, a2, and b1, b2 show local details corresponding to Circle 1 and 2 in Image a and b, respectively.

composite. Similar improvement on tensile strength by addition of functionalized polyolefin elastomers have also been observed on wood flour filled SEBS-g-MA modified PE,<sup>5,7,10,11</sup> PP systems,<sup>14,24</sup> and on EBAGMA modified PP systems.<sup>25</sup> SEM pictures [Fig. 2(b)] showed that the situation in the case of EPR-g-MA is more like the combination of that in Figures 1(b) and 2(a). At the matrix-RS interphase (circles 1 and 2), both good matrix coverage and obvious matrix deformation can be observed. Also, pulled-out trace is fairly unusual [Fig. 1(a)].

Based on these facts, we proposed that the origins of enhanced toughness were different for three com-

patibilizer systems. PE-g-MA toughens composites through improving the matrix-RS interphase bonding, because of the well-known polar interaction and covalently link between anhydride carbonyl and hydroxyl groups of the fiber surfaces,<sup>1-4</sup> as well as their good compatibility with HDPE matrix by PE-end.<sup>5-9</sup> The elastomers or rubber particles dispersed in the matrix control craze growth;<sup>13,26</sup> therefore the impact strength of matrix itself is improved with the presence of EPR. However, the bonding strengths between rubber particles and lignocellulosic fibers, and between matrix and fibers, are still very limited due to lacking of active functional group. Thus, the



**Figure 3** Storage modulus (a) and loss modulus (b) of composites modified by individual compatibilizer as a function of temperature. Compatibilizer content was fixed at 1.5 wt %.

impact stress can still propagate along matrix-fiber interphase rapidly, which is the case in uEPR composites. In the case of EPR-g-MA toughening composites, the modification of rubber with active MA group can offer better bonding strength between rubber (and local matrix) and lignocellulosic fibers. Consequently, it offers more flexible interphase around those lignocellulosic fibers, resulting in more energy absorption during impact fracture.<sup>11,14,24</sup> Both PE-g-MA and EPR-g-MA contain active MA group but the latter seemed not as effective as the former. It is possibly because that grafted MA content in PE-g-MA is slightly higher than that in EPR-g-MA (Table I). Besides, EPR/HDPE/RS composites were actually ternary systems due to containing propylene inside. These differences were more obvious when only 1.5% compatibilizer content was used.

Within each individual compatibilizer, the loading level showed a significant effect on the observed strength properties according to statistical results. For example, in both PE-g-MA and EPR-g-MA systems, more compatibilizers usually led to higher strength which maybe associated with increased MA content. For blends containing uEPR, however, increase of uEPR content made flexural strength decreased and even

lower than that of the control composite. Similar results were reported previously<sup>13,14,27</sup> which were attributed to inferior bulk modulus of added elastomers.

A universal decrease in both tensile and flexural modulus of composites was observed after adding individual compatibilizer, especially PE-g-MA (Table II). However, the reduction of tensile modulus appeared in PE-g-MA system was not dependent on PE-g-MA content, while the other two EPR systems led to more decreased tensile modulus when more compatibilizers were used. It is well-known that tensile modulus is not as sensitive to interfacial interaction as tensile strength is.<sup>6,28,29</sup> Therefore, the reduction appeared in both EPR systems can be associated with the stiffness loss caused by elastomer as one of their intrinsic characteristics. The reductions of flexural modulus were further confirmed by storage modulus experiments [Fig. 3(a)], where the unmodified and PE-g-MA modified composites exhibited the maximum and minimum  $E'$ , respectively, during most temperature range, while the curves of two EPR modified composites were in the middle and fairly close to each other.

The loss modulus, corresponding to viscous modulus of viscoelastic material, offers relaxation transition information of composites. As shown in Figure 3(b), a relaxation transition peak located around 47°C is  $\alpha$ -relaxation point of HDPE. The  $\alpha$ -relaxation points listed in this figure were obtained from approximate peak positions of corresponding smoothed  $E''$  curves. It is known that  $\alpha$ -relaxation is associated with complex multirelaxation process, which was mainly concerned with the molecular motion of PE crystalline region.<sup>30</sup> Also, it indicated that the entire composite started to lose stiffness intensively and was easily deformed when the surrounding temperature reached around 50°C. Obviously,  $\alpha$ -relaxation temperature shifted to higher temperatures after the introduction of RS fiber into HDPE, which may be attributed to the restriction effect brought by fiber on reducing the segmental mobility of polymer molecules at the relaxation temperatures.<sup>31</sup> However, there was no remarkable difference between different composites, which may imply that the restriction effect caused by the compatibilizer is considerably weaker compared to that caused by fiber. The unmodified composite and pure HDPE also exhibited the highest and lowest  $E'$ , which is in agreement with the results obtained from the mechanical test (Table II).

#### Effect of combined compatibilizer systems

The effect of combined PE-g-MA and EPR systems on mechanical properties of composites is summarized in Table III. It was observed that HDPE/RS/PE-g-MA/EPR-g-MA system led HDPE/RS/PE-g-

**TABLE III**  
**Effect of PE-g-MA/EPR Ratio on Mechanical Properties of Resultant HDPE/RS Composites Modified by Combined PE-g-MA and EPRs**

System <sup>a</sup>	Total compatibilizer content <sup>b</sup> (%)	PE-g-MA/EPR ratio	Strength property			Modulus property	
			Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (KJ/m <sup>2</sup> )	Tensile modulus (GPa)	Flexural modulus (GPa)
Control group							
Virgin HDPE			18.9 (0.2)G <sup>c,d</sup>	21.3 (0.1)G	8.12 (0.21)A	0.26 (0.02)F	0.80 (0.01)J
HDPE/RS without compatibilizer			20.3 (0.4)F	31.7 (0.8)F	3.20 (0.14)G	3.36 (0.10)AB	2.72 (0.06)A
HDPE/RS/PE-g-MA/uEPR							
	1.5	2 : 1	21.5 (0.4)E	37.3 (0.7)D	3.82 (0.20)F	3.11 (0.56)BC	1.97 (0.08)G
		1 : 1	23.4 (0.5)CD	32.5 (0.9)F	3.83 (0.17)F	3.29 (0.38)B	2.20 (0.06)DE
	4.3	1 : 2	22.4 (1.1)DE	31.6 (0.6)F	2.89 (0.09)H	3.38 (0.11)AB	2.57 (0.07)B
		2 : 1	24.7 (0.8)B	38.3 (0.7)B	4.81 (0.31)D	2.67 (0.19)E	1.77 (0.01)I
	4.3	1 : 1	23.1 (1.4)CD	38.2 (0.9)BC	4.43 (0.28)E	2.83 (0.16)CDE	2.06 (0.06)F
		1 : 2	23.0 (0.3)CD	37.3 (0.7)D	4.41 (0.22)E	2.57 (0.06)E	2.29 (0.04)C
HDPE/RS/PE-g-MA/EPR-g-MA							
	1.5	2 : 1	21.8 (0.4)E	37.6 (0.3)BCD	3.72 (0.20)F	3.05 (0.19)BCD	2.17 (0.03)DE
		1 : 1	23.9 (0.1)BC	36.1 (0.8)E	4.78 (0.11)D	2.90 (0.45)CDE	2.21 (0.03)D
	4.3	1 : 2	21.6 (0.5)E	35.7 (0.3)E	3.32 (0.09)G	3.66 (0.05)A	2.55 (0.04)B
		2 : 1	25.8 (1.4)A	40.6 (0.1)A	4.99 (0.10)CD	2.78 (0.07)CDE	1.87 (0.02)H
	4.3	1 : 1	26.4 (0.9)A	39.8 (0.4)A	5.50 (0.16)B	2.69 (0.11)DE	1.93 (0.05)HG
		1 : 2	25.6 (0.3)A	37.4 (0.4)CD	5.19 (0.15)C	2.64 (0.28)E	2.13 (0.03)E

<sup>a</sup> HDPE/RS = 60 : 40 (wt %) fixed for all composites.

<sup>b</sup> The content was based on the total composite weight.

<sup>c</sup> Mean values with the same capitalized letter for each property are not significantly different at the 5% significance level.

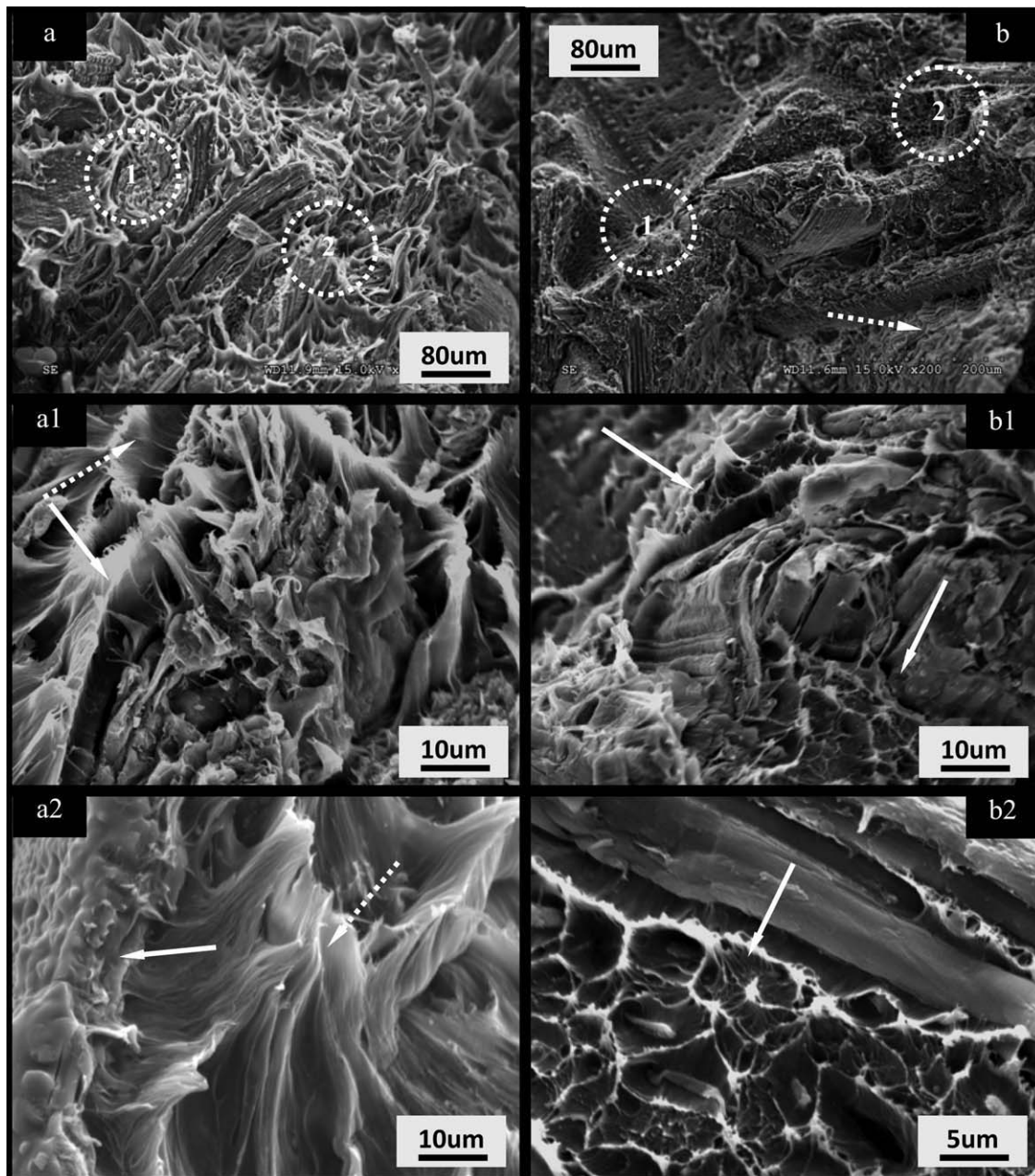
<sup>d</sup> Numbers in the parenthesis are standard deviation based on five specimens.

MA/uEPR system in all three strength properties at almost all PE-g-MA/EPR ratios. Also, the strength properties were improved as the total compatibilizer content increased from 1.5 to 4.3 wt %.

However, the optimum PE-g-MA/EPR ratio seemed different in the two cases. For instance, the ratio of 2 : 1 appeared to be the best for the HDPE/RS/PE-g-MA/uEPR system as revealed by the highest strength value at each of the two total compatibilizer contents. For the HDPE/RS/PE-g-MA/EPR-g-MA system, however, the best ratio was 1 : 1. This phenomenon may be associated with specific individual requirement of two different systems. As discussed in the last section, uEPR failed to improve impact strength effectively at a comparatively low content level due to the absence of effective interphase bonding. Therefore, some interfacial compatibilizer was required by uEPR. Consequently, the impact resistance of its composites was enhanced at higher PE-g-MA percentage because of the superior interphase bonding ability of the latter. SEM micrographs [Fig. 4(a)] also supported this result, where the matrix-RS interphase was obviously improved (solid arrow) as indicated by rare pulled-out trace and good matrix coverage. The combined action of better stress transfer by enhanced interphase bonding and energy absorption by the deformation of local matrix (dashed arrow) led to the best impact strength of the PE-g-MA/uEPR system obtained at

this ratio. Slightly different with the HDPE/RS/PE-g-MA/uEPR system, a balance between interphase enhancement and matrix toughening might be more favorable in the case of HDPE/RS/PE-g-MA/EPR-g-MA system because EPR-g-MA itself contains MA group. The balance might be reached as PE-g-MA/EPR-g-MA ratio was 1 : 1. As shown in Figure 4(b), the corresponding SEM micrographs also presented good interphase bonding (solid arrow). The polymer deformation, however, appeared not as obvious as that shown in Figure 4(a), implying a difference between matrixes of the two systems. It was also observed that tensile and flexural strength values were quite acceptable under the respective best ratio, especially at the total compatibilizer content of 4.3 wt %.

It should be pointed out that under the optimum ratio composites modified by combined compatibilizers showed somewhat better impact strength (Table III) compared to those of the systems modified by either EPR or EPR-g-MA alone (Table II). This is possibly attributed to better interphase bonding brought by the MA group. On the other hand, under the optimum ratio, the combination of PE-g-MA and EPR-g-MA provided composites better tensile and impact strength than PE-g-MA alone, with an acceptable decrease in flexural strength (comparing Tables II with III). These facts implied that a synergistic toughening effect caused by interphase modifier, MA group, and matrix toughener, EPR, together

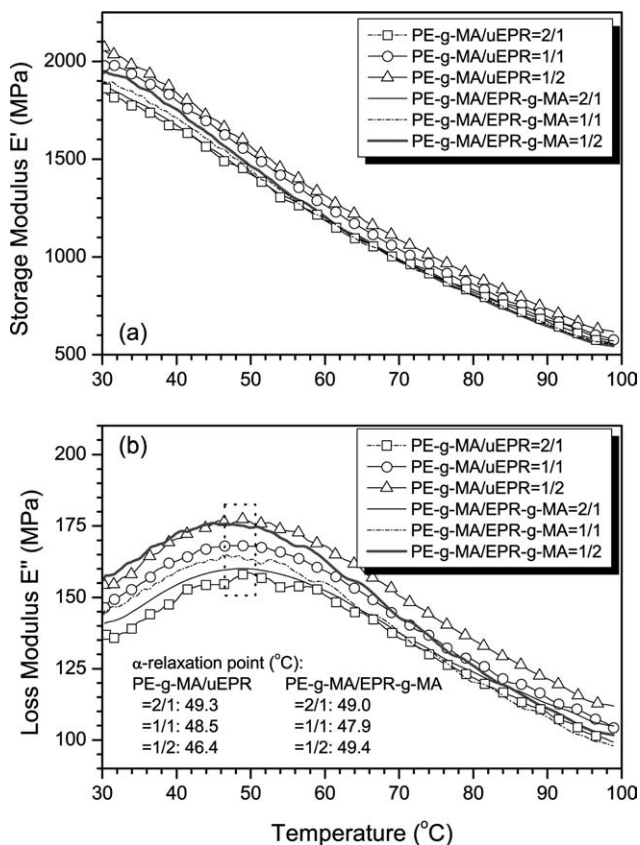


**Figure 4** SEM micrograph of impact-fractured surfaces of composites: (a) modified by PE-g-MA/uEPR and (b) modified by PE-g-MA/EPR-g-MA. Images a1, a2, and b1, b2 show local details corresponding to Circle 1 and 2 in Image a and b, respectively.

was possibly better than a single toughening effect caused by either of these two alone. It is known that, during impact fracture, the impact stress usually concentrates on the weakest points (fillers, matrix, or interphases, whatever is weakest) of a composite and then propagates rapidly to cause failure. Therefore, when strength of each point is balanced, the composite tends to be toughened. As stated earlier, when PE-g-MA and EPR-g-MA reached a specific ratio, the toughness of local matrix and interphase might be balanced, which might cause the observed synergistic effect.

Tensile and flexural moduli of modified composites were decreased compared to the control composite (Table III). Flexural modulus was more sensitive to PE-g-MA/EPR ratio than tensile modulus, probably due to the insensitivity of tensile modulus to interfacial nature. Also, flexural modulus was somewhat improved with increasing EPR percentage to 2/3 in both combined systems. Based on  $E'$  and  $E''$  values, dynamic mechanical results (Fig. 5) supported flexural modulus trend listed in Table III. In addition, the temperature range of  $\alpha$ -relaxation shifted to about 50°C for both combined





**Figure 5** Storage modulus (a) and loss modulus (b) of composites modified by combined compatibilizer as a function of temperature. Total compatibilizer content was fixed at 4.3 wt %.

compatibilizer systems. The comparison between Table II and III showed that, under the optimum ratio, moduli of composites modified by combined compatibilizers were slightly lower than those modified by uEPR and EPR-g-MA alone. However, the combination of PE-g-MA and EPRs provided composites better tensile and flexural modulus than PE-g-MA alone, especially at a total compatibilizer content of 1.5 wt %.

## CONCLUSIONS

Compared with unmodified control, the addition of either PE-g-MA or EPR-g-MA alone enhanced tensile, flexural and impact strengths of resultant composites, while uEPR showed negative effect on both tensile and flexural strengths despite moderate improvement on impact strength. The introduction of each individual modifier decreased composites' tensile and flexural moduli to a different extent. Toughening origin of individual compatibilizer was discussed according to inter-phase morphologies and mechanical properties.

The PE-g-MA/EPR ratio affected mechanical properties of composites modified by combined compatibilizers. The optimum PE-g-MA/EPR ratio was con-

sidered as 2 : 1 and 1 : 1 for PE-g-MA/uEPR and PE-g-MA/EPR-g-MA modified composites, respectively. At the optimum ratio, composites showed better strength and acceptable modulus compared to those modified by either uEPR or EPR-g-MA alone. Also, composites modified by the combined PE-g-MA/EPR-g-MA showed better impact strength than that modified by PE-g-MA alone.

## References

- Kazayawoko, M.; Balatineczand, J. J.; Woodhams, R. T. *J Appl Polym Sci* 1997, 66, 1163.
- Kazayawoko, M.; Balatineczand, J. J.; Matuana, L. M. *J Mater Sci* 1999, 34, 6189.
- Kazayawoko, M.; Balatineczand, J. J.; Sodhi, R. N. S. *Wood Sci Technol* 1999, 33, 359.
- Matuana, L. M.; Balatinecz, J. J.; Sodhiand, R. N. S.; Park, C. B. *Wood Sci Technol* 2001, 35, 191.
- Lai, S. M.; Yeh, F. C.; Wang, Y.; Chanand, H. C.; Shen, H. F. *J Appl Polym Sci* 2003, 87, 487.
- Liang, Q. X.; Matuana, L. M. *J Appl Polym Sci* 2003, 88, 278.
- Wang, Y.; Yeh, F. C.; Lai, S. M.; Chanand, H. C.; Shen, H. F. *Polym Eng Sci* 2003, 43, 933.
- Luand, J. Z.; Wu, Q. L. *Wood Fiber Sci* 2005, 37, 95.
- Lu, J. Z.; Wuand Negulescu, Q. L., II.; *J Appl Polym Sci* 2005, 96, 93.
- Oksman, K. *Wood Sci Technol* 1996, 30, 197.
- Oksmanand, K.; Lindberg, H. *J Appl Polym Sci* 1998, 68, 1845.
- Oksman, K.; Lindbergand, H.; Holmgren, A. *J Appl Polym Sci* 1998, 69, 201.
- Parkand, B. D.; Balatinecz, J. J. *Polym Compos* 1997, 18, 89.
- Oksmanand, K.; Clemons, C. *J Appl Polym Sci* 1998, 67, 1503.
- Rana, A. K.; Mandaland, A.; Bandyopadhyay, S. *Compos Sci Technol* 2003, 63, 801.
- Sombatsompop, N.; Yotinwattanakumtornand, C.; Thongpin, C. *J Appl Polym Sci* 2005, 97, 475.
- Wang, J.; Tung, J. F.; Fuadand, M. Y. A.; Hornsby, P. R. *J Appl Polym Sci* 1996, 60, 1425.
- Dubnikova, I. L.; Berezinaand, S. M.; Antonov, A. V. *J Appl Polym Sci* 2002, 85, 1911.
- Okada, O.; Keskkulaand, H.; Paul, D. R. *Polymer* 2001, 42, 8715.
- Kamel, S. *Polym Adv Technol* 2004, 15, 612.
- Grozdanov, A.; Buzarovska, A.; Bogoeva-Gaceva, G.; Avella, M.; Erricoand, M. E.; Gentile, G. *Agronomy Sustainable Dev* 2006, 26, 251.
- Habibi, Y.; Ei-Zawawy, W. K.; Ibrahimand, M. M.; Dufresne, A. *Compos Sci Technol* 2008, 68, 1877.
- Saheb, D. N.; Jog, J. P. *Adv Polym Technol* 1999, 18, 351.
- Wu, J. S.; Yu, D. M.; Chan, C. M.; Kimand, J. K.; Mai, Y. M. *J Appl Polym Sci* 2000, 76, 1000.
- Kaci, M.; Cimmino, S.; Silvestre, C.; Duraccio, D.; Benhamidaand, A.; Zaidi, L. *Macromol Mater Eng* 2006, 291, 869.
- Mehrabzadehand, M.; Nia, K. H. *J Appl Polym Sci* 1999, 72, 1257.
- Liu, H.; Wu, Q.; Han, G.; Yao, F.; Kojimaand, Y.; Suzuki, S. *Compos Part A: Appl Sci Manuf* 2008, 39, 1891.
- Matuana, L. M.; Woodhams, R. T.; Balatineczand, J. J.; Park, C. B. *Polym Compos* 1998, 19, 446.
- Danyadi, L.; Renner, K.; Szabo, Z.; Nagy, G.; Moczoand, J.; Pukanszky, B. *Polym Adv Technol* 2006, 17, 967.
- Huang, Y. Q.; Jiang, S. L.; Wuand, L. B.; Hua, Y. Q. *Polym Test* 2004, 23, 9.
- Mohanty, S.; Vermaand, S. K.; Nayak, S. K. *Compos Sci Technol* 2006, 66, 538.