OPTIMISING FORMULATION ON WEATHERING RESISTANCE OF RECYCLED POLYPROPYLENE AND RUBBERWOOD FLOUR COMPOSITES

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The usage of wood–plastic composites (WPCs) in exterior environments was primarily concerned on long-term durability and weatherability when exposed to natural weathering. Discoloration, physical and mechanical properties of WPCs are affected by humidity, sunlight and temperature. The properties of WPCs under service conditions were investigated to optimise the mixture ratios of rubberwood flour and recycled polypropylene using D-optimal mixture design. Effects on physical and mechanical properties of components were analysed. Overall composition significantly affected weathering effects on lightness (L*), discoloration (ΔE), hardness, flexural strength, i.e. modulus of rupture (MOR) and modulus of elasticity (MOE), and maximum strain. L*, ΔE, hardness, MOR and MOE increased with fraction of rubberwood flour. At long weathering exposure times, hardness, MOR and MOE decreased. Fraction of maleic anhydride-grafted polypropylene (MAPP) slightly affected L*, hardness and MOR, while increased ultraviolet stabiliser fraction decreased L* and ΔE but decreased flexural properties. Optimal formulation of WPCs, using the Design-Expert software, based on minimum lightness and discoloration, maximum hardness, MOR, MOE and strain was 61.9 wt% recycled polypropylene, 33.9 wt% rubberwood flour, 3.1 wt% MAPP, 0.2 wt% ultraviolet stabiliser and 1.0 wt% lubricant.

Keywords: Wood-plastic composites, mechanical properties, environmental degradation, statistical experimental design

INTRODUCTION

Wood–plastic composites (WPCs) have been widely developed and applied to non-structural applications including automotive industry as door of inner panels and headliners, construction business as decking and fencing, and in infrastructure as marina and boardwalk (Tamrakar et al. 2011). Likewise, WPCs have replaced softwood lumber in some deck building applications due to its improved durability over the latter (Ganguly & Eastin 2009). WPCs offer low cost, low density, recyclability and eco-friendliness with good mechanical properties and can address some environmental issues. However, WPCs can quickly deteriorate with discoloration and their physical and mechanical properties worsen when exposed to natural weathering (Matuana et al. 2001, Fabiyi et al. 2008). Moisture can accelerate photo-oxidation and mechanical property loss in WPCs by swelling wood fibers, facilitating deeper light penetration into the wood and causing cracks in plastic matrix. This reduces flexural strength and modulus by loss of interfacial bonding between natural fibers and matrix (Stark & Matuana 2004, Chaochanchaikul et al. 2013). In addition, WPCs applied in aboveground exterior environments are degraded by ultraviolet (UV) rays in sunlight or in ground contact by biological agents such as fungi and subterranean termites (Mankowski & Morrell 2000, Pilarski & Matuana 2005). The properties of WPCs under service conditions were investigated under the influence of processing method, wood content and type, content of UV stabiliser and pigments (Muasher & Sain 2006, Stark 2006, Homkhiew et al. 2014a). Dark coloured pigments improved colour stability while high moisture absorption decreased the Charpy impact strength (Butylina et al. 2012). Therefore, when a new WPC material is developed, it is important to evaluate the effect of weathering, as this relates to product durability (Pilarski & Matuana 2005, Chaochanchaikul et al. 2013).

Statistical experimental designs including factorial design, mixture design and taguchi method are used to obtain higher accuracy of experimental data (Martinello et al. 2006). However, fractions of components in a mixture formula cannot be changed independently. (Montgomery 2009). A D-optimal mixture experimental design can be applied to elucidate individual effects of components in a mixture and to optimise the formulation of composite materials (Khosrowshahi & Salem 2011). Recent studies of WPCs have employed statistical experimental designs (e.g. Stark & Matuana 2003, Zhao et al. 2008). Mixture designs are widely used in pharmacy and food industries to assess the effects of composition and to find optimal formulation. However, prior studies on weathering of WPCs did not use D-optimal mixture designs except for moisture resistance (Homkhiew et al. 2014b). Hence, the objective of this research was to optimise the mixture ratios of composites made from recycled polypropylene and rubberwood flour using D-optimal mixture design based on experimentally discoloration and flexural degradation. The new information will facilitate informed decision-making regarding manufacture of such composites.

MATERIALS AND METHODS

Materials

Recycled polypropylene pellets, WT170 with a melt flow index of 11 g 10 min^{-1} at 230 °C, were supplied by Withaya Intertrade Co. Ltd from Samutprakarn, Thailand. Rubberwood flour from the cutting process, used as reinforcement, was collected from the dust collector in a local furniture industry in Songkhla, Thailand. Before compounding, the wood flour was sieved through a standard sieve of mesh size 80 (smaller than 180 µm) and dried in an oven at 110 °C for 8 hours. Coupling agent used was maleic anhydride-grafted polypropylene (MAPP) with 8–10% of maleic anhydride, weight average molecular weight of 9100 and number average molecular weight 3900. HALS additive was used as the UV stabiliser and paraffin wax as lubricant.

Mixture experimental design to optimise formulation

A D-optimal mixture experimental design was performed on the Design-Expert software (version 8.0.6) to statistically evaluate the effects of component fractions on colour change and flexural degradation. The identified model was used to optimise the formulations for WPCs which were defined by component fractions (wt%) for recycled polypropylene ($50 \le x_1 \le 70$), rubberwood flour ($25 \le x_2 \le 45$), MAPP ($3 \le x_3 \le 5$), UV stabiliser ($0 \le x_4 \le 1$) and lubricant ($x_5 = 1$). The total number of runs was 20 as shown in (Table 1). There were 15 different formulations and 5 formulations were repeated to determine the reproducibility and variances (Zhao et al. 2008).

Composites processing

The recycled polypropylene and rubberwood flour were melt blended into WPC pellets using twin-screw extruder. Temperature zones of the extruder were defined in the range of 130–170 °C and the screw rotating speed was 70 rpm. WPC panels from the first stage were subsequently produced in the second stage. WPC pellets were dried at 110 °C for 8 hours prior to mixing with MAPP, UV stabiliser and lubricant (Table 1) and fed into the twin-screw extruder through a 9 mm × 22 mm rectangular die and cooled in ambient air (Homkhiew et al. 2014a).

Characterisations on natural weathering testing

The recycled polypropylene/rubberwood flour composite specimens were cut from extrudates and placed on wood exposure racks at a 45° angle according to ASTM (2003), facing in a southerly direction (Chaochanchaikul et al. 2013). All specimens were placed on the roof of a four-floor building in Hat Yai, Songkhla, Thailand for 360 days. The samples were then removed for characterisations after 60 and 360 days. Three testing types were conducted as follows.

(1) Colour measurements: The colour changes of the recycled polypropylene/rubberwood flour composite samples due to weathering effect were measured according to CIE L*a*b* colour scale. L* represents lightness while a* and b* are chromaticity coordinates to represent the red–green and yellow–blue hues respectively. Three replications of each formulation and ageing time were conducted. Discoloration (ΔE) of the specimens was quantitated using equation 1.

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (1)$$

Table 1 Experimental compositions based on mixture experimental design and measured responses (L*, ΔE, hardness, MOR, MOE and maximum strain) at 60 and 360 days

Run no.	Mixture component fraction (wt%)					L*		ΔE		Hardness (shore D)		MOR (MPa)		MOE (GPa)		Max strain (%)	
	x_1	x_2	x_3	x_4	x_5	D60	D360	D60	D360	D60	D360	D60	D360	D60	D360	D60	D360
1	63.9	29.9	4.5	0.7	1.0	75.1	73.0	44.0	42.4	73.9	70.3	39.9	35.6	1.96	1.76	2.72	2.71
2	70.0	25.0	3.0	1.0	1.0	64.4	70.8	35.5	33.5	72.9	69.9	36.4	33.3	1.73	1.57	2.80	2.68
3	50.0	43.0	5.0	1.0	1.0	77.3	75.0	43.0	42.1	74.7	71.9	35.9	33.7	2.29	2.12	1.94	1.90
4	54.9	38.9	4.5	0.7	1.0	75.9	73.9	40.4	38.8	73.9	71.2	40.9	37.3	2.25	1.88	2.41	2.56
5	59.5	34.5	5.0	0.0	1.0	76.0	75.0	41.5	39.8	73.9	71.2	43.4	38.4	2.08	1.92	2.78	2.69
6	55.4	39.9	3.5	0.2	1.0	76.6	74.5	42.7	40.9	75.0	71.6	42.2	39.4	2.33	2.06	2.51	2.75
7	59.5	34.5	4.0	1.0	1.0	75.8	73.8	44.6	39.9	73.9	71.5	39.9	34.8	2.07	1.88	2.60	2.43
8**	59.5	34.5	5.0	0.0	1.0	75.0	73.4	39.3	38.6	73.1	69.6	38.5	36.6	1.89	1.68	2.87	3.02
9	50.0	44.3	4.3	0.5	1.0	77.5	77.0	48.5	44.3	76.1	72.4	40.8	36.7	2.53	2.19	1.90	2.23
10	68.0	25.0	5.0	1.0	1.0	65.3	67.6	34.0	33.7	73.1	69.7	36.5	32.1	1.81	1.64	2.66	2.50
11	50.0	45.0	3.0	1.0	1.0	77.9	71.7	41.5	44.5	74.6	72.7	39.7	33.3	2.51	2.08	2.11	1.88
12**	50.0	43.0	5.0	1.0	1.0	76.1	75.3	45.9	44.3	74.8	71.7	37.1	33.7	2.46	2.08	1.87	1.96
13	60.3	35.3	3.0	0.5	1.0	73.2	71.2	34.3	36.6	73.2	70.6	39.4	35.2	2.03	1.80	2.65	2.58
14	64.9	30.4	3.5	0.2	1.0	73.8	72.8	43.1	42.6	74.4	69.9	40.6	36.5	1.92	1.68	2.94	2.94
15**	70.0	25.0	3.0	1.0	1.0	66.0	68.4	32.6	31.1	72.5	69.2	36.5	32.5	1.72	1.50	2.89	2.90
16	51.0	45.0	3.0	0.0	1.0	76.1	75.3	38.0	40.3	74.3	72.0	46.6	37.0	2.47	1.98	2.37	1.96
17**	51.0	45.0	3.0	0.0	1.0	77.5	74.2	45.7	43.9	74.1	71.9	44.6	39.6	2.53	2.13	2.48	2.48
18**	50.0	45.0	3.0	1.0	1.0	77.1	73.2	47.1	44.0	75.4	72.0	40.4	36.4	2.56	2.25	2.07	2.10
19	70.0	25.0	4.0	0.0	1.0	73.5	71.1	35.7	33.9	71.9	67.9	38.9	36.4	1.68	1.62	3.27	3.02
20	69.0	25.0	5.0	0.0	1.0	74.3	71.8	35.3	32.4	72.2	68.8	40.9	37.0	1.70	1.68	3.44	3.03

**Duplicate experiments, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene x_4 = UV stabiliser, x_5 = lubricant, L* = lightness, ΔE = discoloration MOR = flexural strength, MOE = flexural modulus, D60 = after weathering for 60 days and D360 = after weathering for 360 days

where subscripts 1 and 2 = values of unexposed and exposed recycled polypropylene/rubberwood flour composite specimens respectively.

(2) Hardness and flexural tests: The specimen dimension was approximately 16 mm × 16 mm × 6.5 mm and dried in an oven at 50 °C for 24 hours prior to hardness test. The test was conducted using a mechanical Shore D durometer in accordance with ASTM (1991). For three-point flexural test, the specimen dimension was 4.8 mm × 13 mm × 100 mm and carried out on a universal testing machine at a crosshead speed of 2 mm min^{-1} and a span of 80 mm according to ASTM (1992). Both tests were performed at ambient room temperature of 25 °C with five replications of each formulation. Hardness and flexural properties were measured before and after outdoor exposure of 60 and 360 days.

(3) Morphological analysis: To assess formation of surface cracks, morphological studies were carried out using scanning electron microscope (SEM) with an accelerating voltage of 20 kV. All specimens were sputter-coated with gold to prevent electrical charging during imaging. Image was taken perpendicular to the surface with 100× magnification.

RESULTS AND DISCUSSION

Statistical analysis of response models

Analysis of variance (ANOVA) of the alternative types of response models including linear, quadratic, cubic and special models revealed that all responses after weathering for 60 and 360 days were best fit with linear model except for lightness and maximum strain at 60 days that were best fit with quadratic model. Table 2 tabulates the fitted model for MOE at 60 days as an example. The sequential linear model sums of squares were significant ($p < 0.05$) for only the linear model. The lack of fit was insignificant for

this model and therefore showed it performed well. The adjusted (adj-R^2 = 95.0%) and the predicted (pred-R^2 = 93.3%) coefficients of determination were considerably high and indicated good fit.

The ANOVA and model adequacy indicated significant linear or quadratic terms in models for each response (Table 3). Statistical significance of these terms supplementing linear models of recycled polypropylene, rubberwood flour, MAPP and UV stabiliser is shown. The modelled responses for quadratic term gave significant interactions, for example, between recycled polypropylene and MAPP and rubberwood flour and MAPP for lightness at 60 days as well as between recycled polypropylene and rubberwood flour for maximum strain at 60 days. This proved that the regression models fitted the data well.

After 60 days, coefficients of determination (R^2) value of the 12 response fits gave the lowest discoloration (65.3%) and the highest maximum strain (97.5%) (Table 3). This indicated that only 34.7 and 2.5% of the experimental variations were not explained by the models. Likewise, the adj-R^2 and pred-R^2 values ranged from 58.8 to 95.2% and from 51.2 to 93.3% respectively, suggesting good fits. The coefficients of variation (CV) of all response fits, used to measure the residual variation in the data, ranged from 0.70 to 7.64%. The CV values were considerably low and indicated good precision in determining characteristics of the material.

Table 2 Fitted model summary for flexural modulus at 60 days

Source	Sequential p-value	Lack of fit p-value	Adj-R^2 (%)	Pred-R^2 (%)	
Linear	0.00	0.81	95.0	93.3	Suggested
Quadratic	0.27	0.96	95.8	91.7	
Special cubic	0.90	0.95	93.9	90.1	
Cubic	0.95	-	92.7	-	Aliased

p-value less than 0.05 is considered significant; Adj-R^2 = adjusted coefficient of determination, Pred-R^2 = predicted coefficient of determination

Table 3 Analysis of variance and model adequacy for L*, ΔE, hardness, flexural strength, flexural modulus and maximum strain responses

Source	L*		ΔE		Hardness		MOR		MOE		Max strain	
	D60	D360	D60	D360	D60	D360	D60	D360	D60	D360	D60	D360
Model	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Linear mixture	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
x_1x_2	0.11										0.03	
x_1x_3	0.03										0.84	
x_1x_4	0.53										0.08	
x_2x_3	0.04										0.91	
x_2x_4	0.59										0.09	
x_3x_4	0.87										0.05	
Lack of fit	0.08	0.27	0.09	0.09	0.10	0.86	0.63	0.79	0.81	0.89	0.07	0.78
R^2(%)	94.5	72.5	65.3	71.0	71.1	88.2	71.4	74.4	95.8	88.7	97.5	81.3
Adj-R^2(%)	89.5	67.3	58.8	65.6	65.7	86.0	66.0	69.5	95.0	86.6	95.2	77.8
Pred-R^2(%)	64.9	54.8	51.2	58.4	59.2	81.3	55.5	60.9	93.3	82.3	84.0	69.3
CV(%)	1.80	1.84	7.64	6.57	0.85	0.70	4.10	3.34	3.34	4.45	3.70	7.34

p-value less than 0.05 is considered significant; L* = lightness, ΔE = discoloration, MOR = flexural strength, MOE = flexural modulus, D60 = after weathering for 60 days, D360 = after weathering for 360 days, R^2 = coefficients of determination, Adj-R^2 = adjusted coefficient of determination, Pred-R^2 = predicted coefficient of determination, CV = coefficient of variation, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene x_4 = UV stabiliser

Model adequacy

The good linear fit for residuals of MOE after weathering for 60 days indicated that the residuals were close to normally distributed (Figure 1a). Normally-distributed residuals are a requirement for validity of least squares regression, and this condition is satisfied. There was no indication of possible outliers such as faulty experiment cases with particularly large residuals. There was no obvious linear or exponential pattern for plot of residuals vs predicted values (Figure 1b). If the residuals had such obvious pattern, the model would not be appropriate (Montgomery 2009). The model outputs fit the actual observations quite well, with MOE D60 model deviating from actual by less than 10% (Figure 1c). These adequacy checks of the MOE D60 response model indicated good fit to data. Similar checking for the other modelled responses gave no indications of problems with the fitted models either.

Effect of mixing composition on lightness

Regression fits for lightness after weathering for 60 and 360 days were:

$$L^*\ D60 = 70.79x_1 + 76.16x_2 - 793.51x_3 + 1053.12x_4 + 6.91x_1x_2 + 982.79x_1x_3 - 1158.85x_1x_4 + 957.41x_2x_3 - 989.52x_2x_4 - 268.09x_3x_4 \quad (2)$$

$$L^*\ D360 = 70.49x_1 + 75.45x_2 + 68.00x_3 + 37.33x_4 \quad (3)$$

where L* = lightness, D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene and x_4 = UV stabiliser.

The coefficients for fractions of recycled polypropylene, rubberwood flour and UV stabiliser were positive. Rubberwood flour had larger coefficients than recycled polypropylene due to high photobleaching of the wood components, particularly lignin (Stark & Matuana 2006). The covered experimental regions of L* D60 and L* D360 are shown in Figures 2a and b respectively. The three components (recycled polypropylene, rubberwood flour and MAPP) are represented by the corners in these triangular plots. The additives, including UV stabiliser and lubricant, were fixed at 0.5 and 1 wt% respectively. Contours in the coloured areas show the L* D60 and L* D360 regression fits varying from 70 to 78 and 71 to 75 respectively. Lightness increased with rubberwood flour content. With increased rubberwood flour fraction in the composites, more wood flour was exposed at the sample surface where complete encapsulation by the matrix was less likely to occur (Adhikary 2008). Recycled polypropylene/rubberwood flour composites weathered for 60 days had lighter colour after 360 days. Colour change of composites occurred in three stages. The composites quickly lightened after weathering for 60 days and then darkened again with further exposure. Homkhiew et al. (2014a) found that after approximately 180 days WPC samples were again lightened by exposure to weathering. In addition, high fractions of MAPP at 3–5 wt% gave greater lightness. This may be caused by weakened interfacial adhesion at

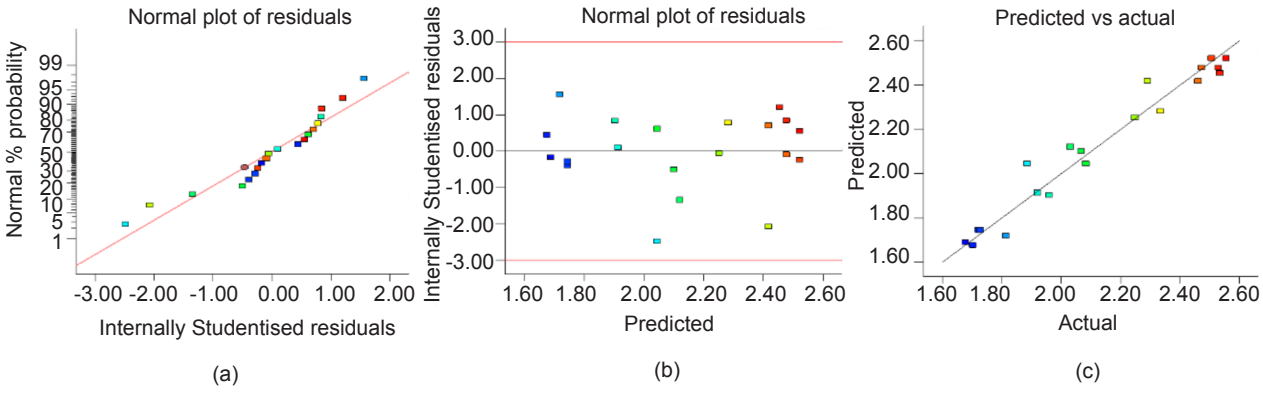


Figure 1 Model adequacy checking for flexural modulus after exposure for 60 days; (a) normal probability plot of residuals, (b) plot of residuals vs predicted values and (c) plot of predicted vs actual values

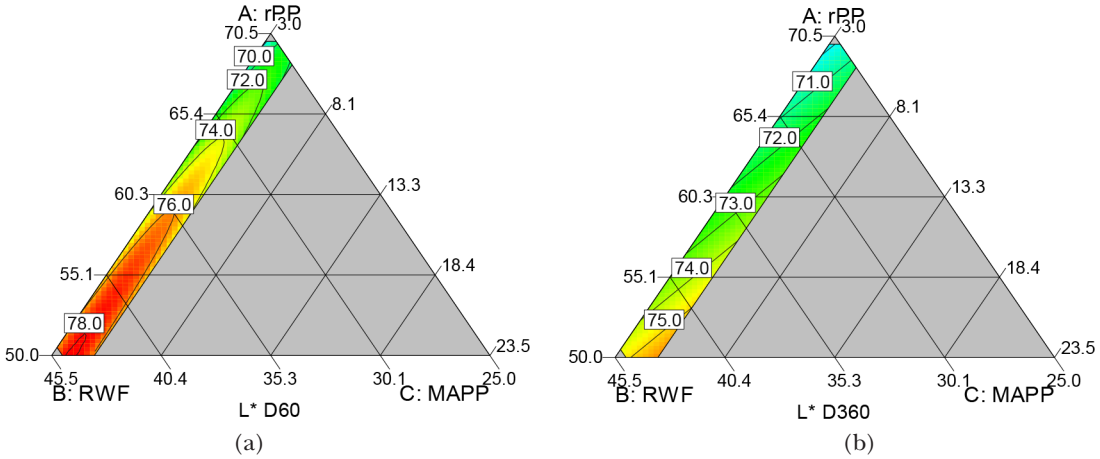


Figure 2 Triangular contour plots for effects of the composition on lightness at (a) 60 and (b) 360 days, with UV stabiliser fixed at 0.5 wt% and lubricant at 1 wt%; rPP = recycled polypropylene, RWF = rubberwood flour, MAPP = maleic anhydride-grafted polypropylene, L* = lightness, D60 = after weathering for 60 days, D360 = after weathering for 360 days

high MAPP contents. The photodegradation of wood components on the surface of the composites was accelerated by weak adhesion between the wood flour and plastic matrix (Stark & Matuana 2004, Matuana et al. 2011). Adding 1 wt% UV stabiliser decreased lightness of the recycled polypropylene/rubberwood flour composites. This may be attributed to UV stabiliser, i.e. HALS preventing photodegradation of polymer (Muasher & Sain 2006). The optimal composition, based on these model fits are shown in Figure 3. The model-based optimal formulation is shown in Table 4 with minimum lightness at 70 wt% recycled polypropylene, 25 wt% rubberwood flour, 3 wt% MAPP, 1 wt% UV stabiliser and 1 wt% lubricant, with a high desirability score of 0.908, generated to balance the optimisation of two models.

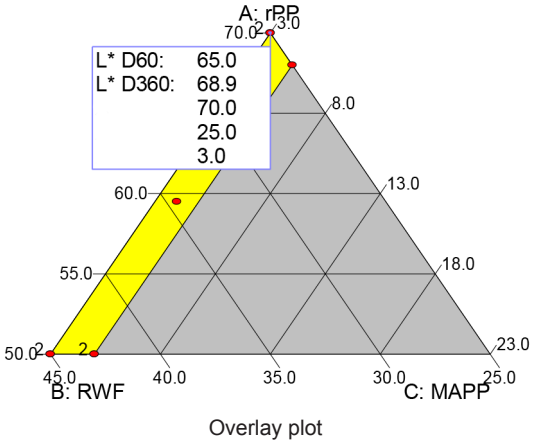


Figure 3 Optimal formulation for lightness; rPP/x_1 = recycled polypropylene, RWF/x_2 = rubberwood flour, MAPP/x_3 = maleic anhydride-grafted polypropylene, L* = lightness, D60 = after weathering for 60 days, D360 = after weathering for 360 days

Effect of mixing composition on discoloration

Linear regression models for discoloration after weathering for 60 and 360 days were:

$$\Delta E\ D60 = 34.68x_1 + 45.29x_2 + 50.19x_3 + 44.67x_4 \quad (4)$$

$$\Delta E\ D360 = 33.67x_1 + 43.66x_2 + 44.73x_3 + 39.09x_4 \quad (5)$$

where ΔE = discoloration, D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene and x_4 = UV stabiliser.

The coefficients decreased with exposure time, indicating reduced discoloration. ΔE at 360 days (range of 36 to 42) increased for high fractions of wood flour (Figure 4). The reason for this phenomenon was probably similar as described earlier, namely, exposure of wood flour at the sample surface (Adhikary 2008). The choice of MAPP content between 3 and 5 wt% barely affected discoloration of composites at 360 days. The optimal formulation for ΔE based on these numerical models and the desirability score for this combined optimisation, are given in Table 4.

Table 4 Predicted optimal formulations and their responses from multiobjective optimisations

Property	Mixture component fraction (wt%)					Predicted response		Desirability
	x_1	x_2	x_3	x_4	x_5	D60	D360	
L*	70.0	25.0	3.0	1.0	1.0	65.0	68.9	0.908
ΔE	69.8	25.0	3.2	1.0	1.0	35.3	34.0	0.809
Hardness (shore D)	50.0	45.0	3.0	1.0	1.0	75.1	72.5	0.853
MOR (MPa)	51.9	43.4	3.4	0.2	1.0	43.0	37.9	0.713
MOE (GPa)	50.0	45.0	3.0	1.0	1.0	2.52	2.12	0.892
Max strain (%)	69.0	25.0	4.9	0.1	1.0	3.23	3.09	0.931

L* = lightness, ΔE = discoloration, MOR = flexural strength, MOE = flexural modulus, D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = MAPP, x_4 = UV stabiliser, x_5 = lubricant

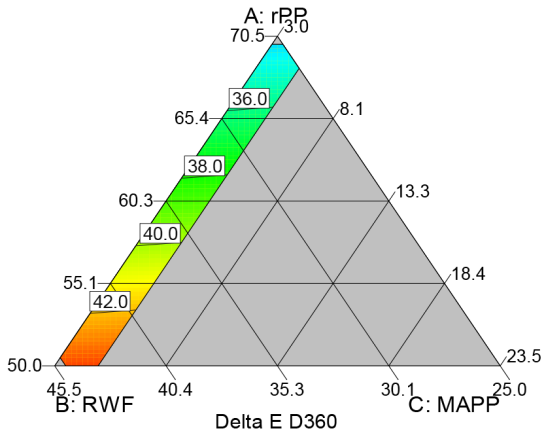


Figure 4 Triangular contour plots for effects of composition on discoloration (ΔE) at 360 days, with UV stabiliser fixed at 0.5 wt% and lubricant at 1 wt%; rPP = recycled polypropylene, RWF = rubberwood flour, MAPP = maleic anhydride-grafted polypropylene, D360 = after weathering for 360 days

Effect of mixing composition on hardness

Linear regression fits for hardness after 60 and 360 days exposure were:

$$\text{Hardness D60} = 72.37x_1 + 74.74x_2 + 74.30x_3 + 81.46x_4 \quad (6)$$

$$\text{Hardness D360} = 68.87x_1 + 72.03x_2 + 68.38x_3 + 82.51x_4 \quad (7)$$

where D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene and x_4 = UV stabiliser.

The coefficients of recycled polypropylene rubberwood flour and MAPP decreased with increasing exposure times from 60 to 360 days because polymer chain scission which resulted in surface cracks as well facilitated the removal of degraded wood component through the cracks (Matuana et al. 2011). In addition, chain scissions accumulated over the exposure time (Du et al. 2010). The UV stabiliser fraction had the largest positive coefficients in the model fits because, as free radical scavenger, it prevented photodegradation in plastics (Muasher & Sain 2006). Hardness at 360 days increased with rubberwood flour fraction (Figure 5). Rubberwood filler has considerably higher hardness than weak polymer matrix (Homkhiew et al. 2015), so flexibility is reduced by increase in rubberwood flour content, resulting in more rigid composites (Rahman et al. 2009). The addition of MAPP from 3 to 5 wt% increased the hardness of composites. An optimal formulation for hardness, based on the numerical models, is shown in Table 4.

Effect of mixing composition on flexural strength

Linear regression models fitted for flexural strength at 60 and 360 days were:

$$\text{MOR D60} = 41.54x_1 + 44.64x_2 + 25.13x_3 - 51.72x_4 \quad (8)$$

$$\text{MOR D360} = 36.96x_1 + 38.92x_2 + 35.59x_3 - 45.41x_4 \quad (9)$$

where MOR = flexural strength, D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene and x_4 = UV stabiliser.

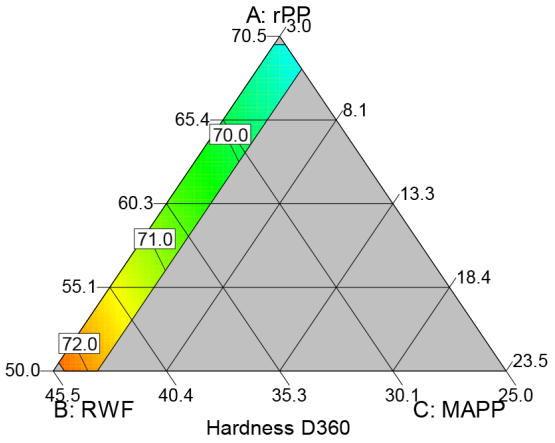


Figure 5 Triangular contour plots for effects of composition on hardness at 360 days, with UV stabiliser fixed at 0.5 wt% and lubricant at 1 wt%; rPP = recycled polypropylene, RWF = rubberwood flour, MAPP = maleic anhydride-grafted polypropylene, D360 = after weathering for 360 days

The fraction of rubberwood flour has the largest positive coefficients in the fitted models for MOR, so flexural strength increased with increase in fraction of rubberwood flour. In contrast, MOR decreased with the increase in fraction of UV stabiliser and has negative coefficient, so UV stabiliser fraction should be minimised. This is probably due to non-homogeneous spatial distribution of wood flour, polymer and UV stabiliser (Wechsler & Hiziroglu 2007). The contours in the coloured areas represent MOR at 60 and 360 days with values varying from 38 to 42 MPa and 35 to 36.5 MPa respectively (Figure 6). MOR at 60 days increased with rubberwood flour content. This is due to the reinforcing effect of the wood flour in continuous plastic matrix (Mohanty et al. 2004). At 360 days, increase in MOR as rubberwood flour content increased was not significant. This showed that, with the longer exposure, loss of MOR increased with increasing rubberwood flour content. When WPCs were exposed to water, the swelling of wood flour caused microcracks in the matrix and thus the efficiency of stress transfer from wood flour to plastic matrix decreased (Stark & Matuana 2006). MOR of the composites reduced with exposure time due to decreasing molecular weight and an increase of polymer chain scission and cracking in WPCs (Li et al. 2012). These results are also presented in SEM micrographs (Figure 7). The composites with 25 wt% rubberwood flour (Figure 7a) had less rubberwood flour on the surface than composites with 45 wt% rubberwood flour (Figure 7c). Recycled polypropylene/rubberwood flour composites exposed for 360 days (Figures 7b and d) showed large surface cracking due to polymer chain scission, which resulted from cycles of wetting and drying (Fabiyi et al. 2008). The composites with 25 wt% rubberwood flour (Figures 7b) displayed less surface cracking than the composites with 45 wt% rubberwood flour (Figures 7d). When WPCs were exposed to water, the swelling increased with increase in rubberwood flour content and led to increased cracking (Stark & Matuana 2006). The optimal composition based on linear regression models is tabulated in Table 4.

Effect of mixing composition on flexural modulus

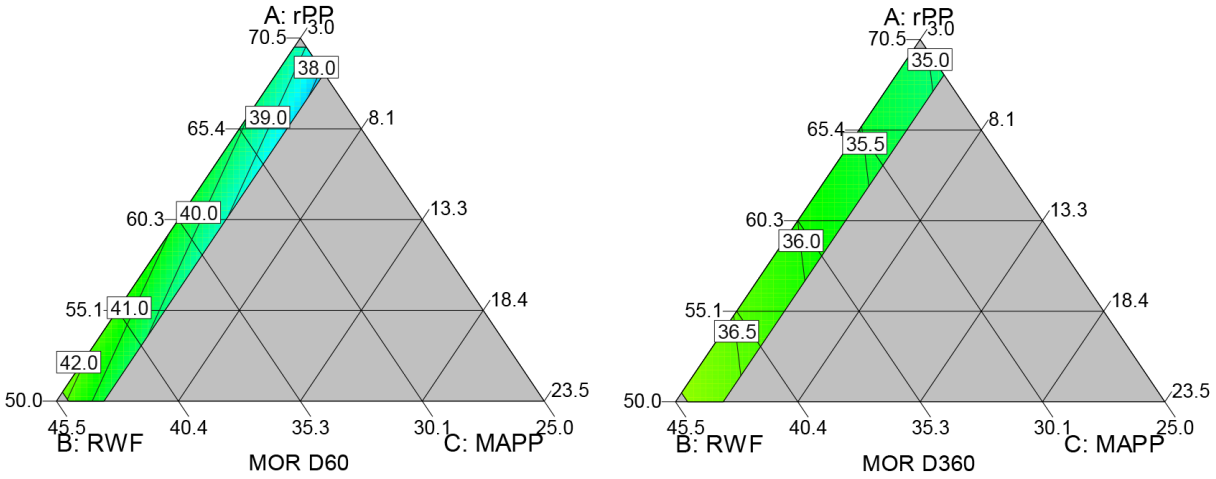
The linear regression models fitted for flexural modulus at 60 and 360 days were:

$$\text{MOE D60} = 1.70x_1 + 2.52x_2 + 1.43x_3 + 2.61x_4 \quad (10)$$

$$\text{MOE D360} = 1.54x_1 + 2.11x_2 + 2.10x_3 + 2.21x_4 \quad (11)$$

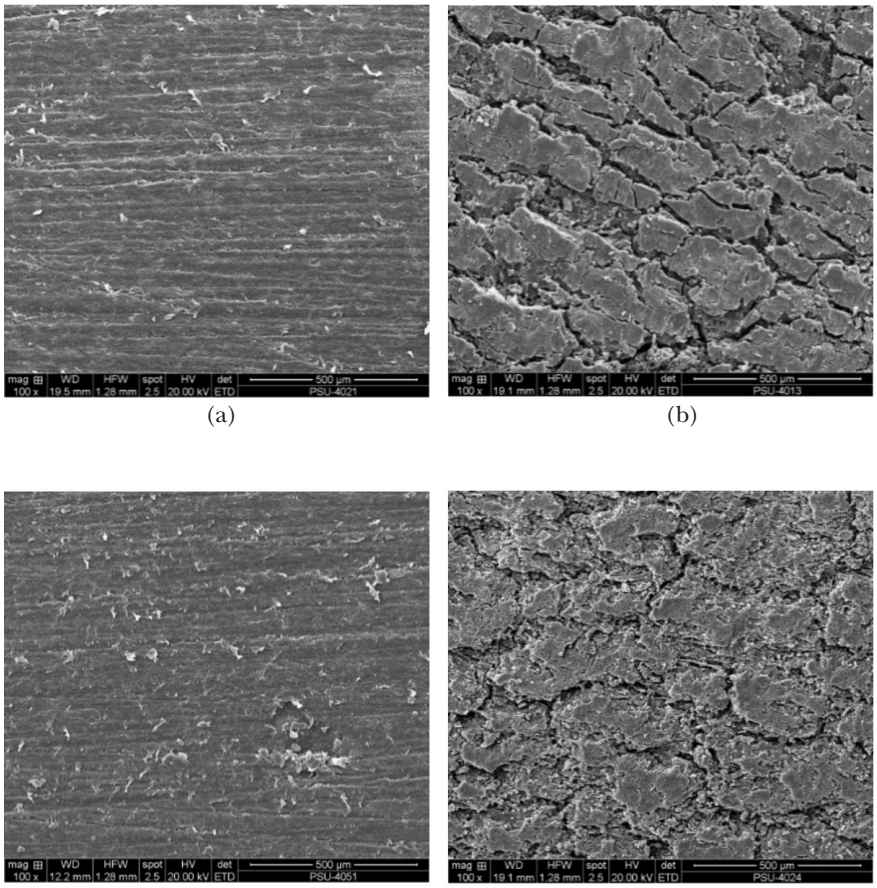
where MOE = flexural modulus, D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene and x_4 = UV stabiliser.

By these equations, all component fractions, namely, recycled polypropylene rubberwood flour MAPP and UV stabiliser increased the MOE after weathering for 60 and 360 days; all terms containing these variables had positive coefficients. UV stabiliser fraction had the largest coefficient in each fit. Furthermore, the coefficients of recycled polypropylene, rubberwood flour and UV stabiliser decreased with longer exposure times. The swelling of wood cell walls when penetrated by water facilitates light penetration and contributes to degradation of mechanical properties (Stark & Matuana 2006). The UV stabiliser could not protect against water absorption which may have contributed more to degradation than UV exposure. UV photodegradation may mainly affect the WPCs on the sample surface (Chaochanchaikul & Sombatsompop 2011). In addition, rubberwood



(a) (b)

Figure 6 Triangular contour plots for effects of composition on flexural strength (MOR) at (a) 60 and (b) 360 days, with UV stabiliser fixed at 0.5 wt% and lubricant at 1 wt%; rPP = recycled polypropylene, RWF = rubberwood flour, MAPP = maleic anhydride-grafted polypropylene, MOR = flexural strength, D60 = after weathering for 60 days, D360 = after weathering for 360 days



(a) (b)

(c) (d)

Figure 7 SEM (100×) images of wood–plastic composites surfaces before (left column) and after exposure for 360 days (right column): recycled polypropylene composites with (a and b) 25 wt% rubberwood flour and (c and d) 45 wt% rubberwood flour

flour has higher coefficients than recycled polypropylene. This implied that rubberwood flour contributed more to MOE than recycled polypropylene, because wood flour was stiffer than the plastic. The optimal composition based on these linear regression models is given in Table 4.

Effect of mixing composition on maximum strain

The regression fits for maximum strain after exposures for 60 and 360 days were:

$$\text{Maximum strain D60} = 3.31x_1 + 2.30x_2 - 2.02x_3 + 222.05x_4 + 0.69x_1x_2 + 5.90x_1x_3 - 240.37x_1x_4 + 3.14x_2x_3 - 234.86x_2x_4 - 248.36x_3x_4 \quad (12)$$

$$\text{Maximum strain D360} = 3.16x_1 + 2.36x_2 + 2.69x_3 - 5.36x_4 \quad (13)$$

where D60 = after weathering for 60 days, D360 = after weathering for 360 days, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = maleic anhydride-grafted polypropylene and x_4 = UV stabiliser.

The fraction of recycled polypropylene had larger positive coefficients than rubberwood flour in the fit, so maximum strain increased with high fraction of recycled polypropylene. Increasing exposure time reduced the coefficient of recycled polypropylene because it became more brittle with weathering, whereas the coefficient of rubberwood flour grew with exposure time. Wood flour absorbed water during exposure, and this led to softening of the WPCs (Chaochanchaikul & Sombatsompop 2011). The optimal formulation based on these numerical models is shown in Table 4.

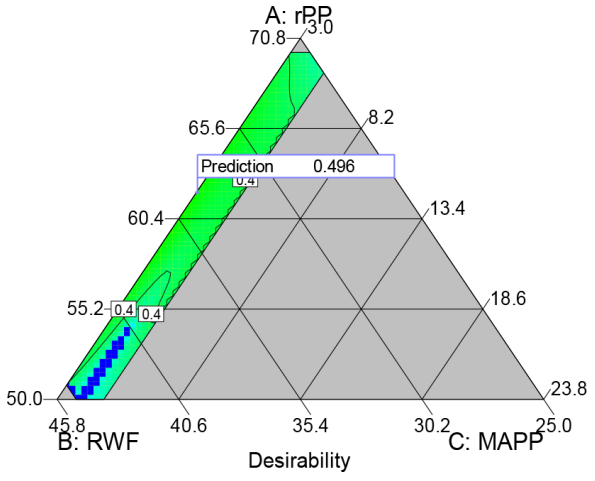


Figure 8 Optimal formulation for overall desirability; rPP = recycled polypropylene, RWF = rubberwood flour, MAPP = maleic anhydride-grafted polypropylene

Optimal overall resistance to natural weathering

An optimal formulation for recycled polypropylene/rubberwood flour composites was achieved with regard to the minimum lightness and discoloration as well as maximum hardness, flexural strength and strain. All regression models were performed with the Design-Expert software under the multiobjective optimisation. The optimal formulation was 61.85 wt% recycled polypropylene, 33.85 wt% rubberwood flour, 3.1 wt% MAPP, 0.2 wt% UV stabiliser, and 1.0 wt% lubricant (Figure 8). The optimal formulation with the predicted responses is tabulated in Table 5.

CONCLUSIONS

Mixture experimental design, statistical modelling and response surface methodology were used to determine the influences of recycled polypropylene/rubberwood flour composite formulation and to optimise the formulation for weathering resistance. ANOVA indicated that all component fractions varied, namely, recycled polypropylene, rubberwood flour, MAPP and UV stabiliser significantly affected lightness, discoloration, hardness, flexural strength and modulus and maximum strain. Generally, high fraction of rubberwood flour increased L* and ΔE across exposure times. When composites were exposed to natural weathering for 60 and 360 days, high fractions of rubberwood flour increased hardness, MOR and MOE but reduced maximum strain. However, hardness, MOR and MOE clearly reduced with exposure time. The MAPP slightly affected L*, hardness and MOR, which increased with MAPP content. The fraction of UV stabiliser also had positive effects on the L* and ΔE because it prevented photodegradation of polymer. This study demonstrated that design and analysis of mixture experiments were efficient methods to optimise the formulation of recycled polypropylene/rubberwood flour composites for minimum colour changes and maximum hardness and flexural properties.

Table 5 Predicted responses with formulation optimised jointly for all properties

Property	Mixture component fractions (wt%)					Predicted response	
	x_1	x_2	x_3	x_4	x_5	D60	D360
L*	61.85	33.85	3.1	0.2	1.0	74.2	72.3
ΔE						39.3	38.0
Hardness (shore D)						73.5	70.3
MOR (MPa)						42.0	37.1
MOE (GPa)						2.05	1.79
Max. strain (%)						2.90	2.75

L* = lightness, ΔE = discoloration, MOR = flexural strength, MOE = flexural modulus, x_1 = recycled polypropylene, x_2 = rubberwood flour, x_3 = MAPP, x_4 = UV stabiliser, x_5 = lubricant, D60 = after weathering for 60 days, D360 = after weathering for 360 days

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