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Optimal formulation of recycled polypropylene/rubberwood flour composites on hardness property

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Abstract. Mixture experimental design was applied to determine the optimal mixture for composites between rubberwood flour (RWF) and recycled polypropylene (rPP). Experiments were conducted based on a D-optimal mixture design and analyzed using response surface methodology. Analysis of variance revealed that compositions including rPP, RWF, maleic anhydride grafted polypropylene (MAPP), and ultraviolet (UV) stabilizer significantly affected hardness property. Contour plots of the response surface demonstrated that an increase of RWF content steadily enhanced hardness value, but hardness property sharply decreased with an increase of rPP loading. An addition of the UV stabilizer in the composites showed a slight decrease of the hardness value. This result recommends that amount of UV stabilizer used should be minimized. With this experimental design, the optimal formulation of rPP/RWF composites found was 50.0 wt% rPP, 45.0 wt% RWF, 3.9 wt% MAPP, 0.1 wt% UV stabilizer, and 1.0 wt% Lubricant.

Introduction

Natural fibers from maple, oak, pine, and rubberwood are reinforcement materials, which have been extensively popularized and used in composite industries. It was used as a replacement for synthetic fillers such as glass fiber, carbon fiber, and inorganic filler. Compared to these materials, natural fibers provide low cost, low density, recyclability, and their non-abrasive natures. A large amount of natural fibers (wood wastes) is generated at different processing in wood applications such as in sawmills and in furniture making [1]. The wastes in the form of flour, sawdust, and chips have primary been used as inexpensive filler in composites. In addition, an increase of plastic production and consumption results in plastic wastes to be the major constituent of municipal solid waste; however, it is a promising raw material for producing wood-plastic composites (WPCs) [2, 3]. The use of recycled plastics for producing WPCs would not only offer a safe and effective disposal of plastic wastes, but also reduces the consumption of natural resources [4, 5]. Therefore, increasing the use of recycled plastics by blending with wood wastes provides the chance of lessening wastes going to landfill, decreasing solid waste disposals, and reducing the costs of making the WPCs [1, 6].

Applications and end-products of WPCs, such as decking and part of cars, have made. It is necessary to evaluate hardness characteristic of such materials. Because the hardness property is a measurement of the wear resistance, and harder materials resist a better friction and wear [7]. Thereby, the hardness property has to be taken into account in the design of WPCs for final products.

Nowadays, most of the experiment on composite formulations is still conducted by changing the contents of each composition at a time, and the other compositions are constantly fixed in order to investigate the effects of such specific composition. Mixture experimental design by using D-optimal is an important method to mediate an effect on the dependent compositions of interest [8]. It also decreases the number of experiments but increases the scientific information of compositions, which are the important values to determine the mathematical equation for improving the properties of end-products [9, 10]. Therefore, the D-optimal mixture experimental design was applied to determine the model parameters in WPCs. The main purposes of present research were to investigate the effect of compositions and to determine the optimal mixture ratios by designing mixture experiment for composites from recycled polypropylene and rubberwood flour based on hardness property.

Experimental

Materials

Recycled polypropylene (rPP) pellets were purchased from Withaya Intertrade Co., Ltd (Samutprakarn, Thailand). Rubberwood flour (RWF) was supplied from local furniture factory (Songkhla, Thailand). Maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent, manufactured by Sigma-Aldrich (Missouri, USA). It contains 8-10% of maleic anhydride. Hindered amine light stabilizer (MEUV008) was purchased from TH Color Co., Ltd (Samutprakarn, Thailand), chosen as ultraviolet (UV) stabilizer. Paraffin wax was procured from Nippon Seiro Co., Ltd (Yamaguchi, Japan), used as lubricant (Lub).

Experimental design to optimize formulation

Mixture experimental design was used to study the hardness property of rPP/RWF composites using Design Expert software (version 8.0.6, Stat-Ease, Inc., Minneapolis, USA), according to a D-optimal design. In mixture experiments, the components are the variables of mixture, and their levels cannot be changed independently [11]. When interesting region for experiment is not a simplex due to irregular experiment region [11], D-optimal design is appropriate method to statistically evaluate the effect of compositions and to optimize the formulation. The rPP (x_1), RWF (x_2), MAPP (x_3), and UV stabilizer (x_4) were four key variables studied, while the hardness was the variable response obtained in the study. The intervals selected to conduct the experiment design were: 50-70 wt% rPP, 25-45 wt% RWF, 3-5 wt% MAPP, 0-1 wt% UV stabilizer, and 1 wt% Lub. The design included 15 formulations and 5 replications to evaluate lack of fit. Thus, the total number of runs was 20 in Table 1.

Table 1 Experimental compositions and response based on mixture experimental design

Experiment run No.	Mixture Proportion (wt%) x_1	x_2	x_3	x_4	x_5	Hardness (Shore D)	Experiment run No.	Mixture Proportion (wt%) x_1	x_2	x_3	x_4	x_5	Hardness (Shore D)
1	63.9	29.9	4.5	0.7	1.0	73.3 (0.40)**	11	50.0	45.0	3.0	1.0	1.0	75.2 (0.19)
2	70.0	25.0	3.0	1.0	1.0	73.2 (0.17)	12*	50.0	43.0	5.0	1.0	1.0	74.9 (0.44)
3	50.0	43.0	5.0	1.0	1.0	74.8 (0.38)	13	60.3	35.3	3.0	0.5	1.0	74.3 (0.39)
4	54.9	38.9	4.5	0.7	1.0	75.5 (0.40)	14	64.9	30.4	3.5	0.2	1.0	74.6 (0.10)
5	59.5	34.5	5.0	0.0	1.0	74.6 (0.53)	15*	70.0	25.0	3.0	1.0	1.0	72.9 (0.37)
6	55.4	39.9	3.5	0.2	1.0	74.7 (0.46)	16	51.0	45.0	3.0	0.0	1.0	76.1 (0.09)
7	59.5	34.5	4.0	1.0	1.0	74.9 (0.60)	17*	51.0	45.0	3.0	0.0	1.0	75.8 (0.24)
8*	59.5	34.5	5.0	0.0	1.0	75.0 (0.39)	18*	50.0	45.0	3.0	1.0	1.0	74.9 (0.33)
9	50.0	44.3	4.3	0.5	1.0	75.3 (0.51)	19	70.0	25.0	4.0	0.0	1.0	73.6 (0.36)
10	68.0	25.0	5.0	1.0	1.0	73.7 (0.26)	20	69.0	25.0	5.0	0.0	1.0	73.8 (0.19)

Note; *duplicate experiments, ** the values in parentheses are standard deviations from five replications.

Preparation of wood-plastic composites

Before compounding, RWF was sieved through a standard sieve of 80 mesh size and dried in an oven at 110 ^{o}C for 8 h. RWF and rPP were then mixed into WPC pellets by using a twin-screw extruder (Model SHJ-36 from En Mach Co., Ltd, Nonthaburi, Thailand). The extruding temperature ranged from 130^{o}C to 170 ^{o}C to reduce degradation of the compositions. After compounding, the WPC panels were also prepared. WPC pellets, MAPP, UV stabilizer, and lubricant were dry-mixed and added into feeder of the twin-screw extruder according to the compositions given in Table 1. The 10 temperature zones of extruder were set to profile in range of 130-190 ^{o}C, while the screw rotating speed was controlled at 50 rpm. The samples were then extruded through a 9 mm × 22 mm rectangular die and cooled in atmospheric air. Consequently, the specimens were machined following the standard of American Society for Testing and Materials (ASTM) for hardness test.

Composite characterization

Hardness measurement of the composites was tested according to ASTM D2240 standard by using mechanical Shore D Durometer (Model GS-702G from teclock corporation, Nagano, Japan). The rectangular specimens with dimensions of 16 mm × 16 mm × 6.5 mm were tested. The test was characterized at room temperature (25 ^{o}C). Average of five specimens was measured and calculated.

Results and Discussion

Statistical analysis of response surface model

The statistical significance of linear model was analyzed by analysis of variance (ANOVA), as given in Table 2. The results revealed that the model was statistically significant at 5% significance level, indicating by p-value less than α (α = 0.05). This result indicates that at least one of the four variables contributes the hardness response. For the linear mixture, variables of rPP, RWF, MAPP, and UV stabilizer significantly affect hardness property. In addition, the ANOVA also showed that lack of fit was not significant for the model. This concludes that the regression model fits the data.

Table 2 Analysis of variance and model adequacy for hardness of rPP/RWF composites

Response	Model	Linear mixture	Lack of fit	R^2	Adj-R^2	Pred-R^2	CV %
Hardness	<0.0001*	<0.0001*	0.0510	0.8336	0.8024	0.7663	0.53

**P*-value less than 0.05 is considered significant.

The fit of the model was also checked by determination coefficient (R^2), adjusted determination coefficient (adj-R^2), predicted determination coefficient (pred-R^2), and coefficient of variation (CV). The R^2 value of hardness (0.8336) reveals that about 83.36% of variability in observation is explained by the four key compositions of composites, whereas only 16.64% of the total variability couldn't be explained. A closer to 1 of R^2 value indicates good fits [12]. Also the adj-R^2 value of hardness (0.8024) is large and very close to the ordinary R^2. This indicates that there is a less chance of insignificant terms included in the model [13]. The pred-R^2 value of hardness was 0.7663 meaning that this model could be expected to explain about 76.63% of the variability in predicting new data. This result also revealed that pred-R^2 of 0.7663 is in reasonable agreement with the adj-R^2 of 0.8024. At the same time, the coefficient of variation found was 0.53%. The low value of CV indicates the good relative dispersion of the experimental points from the predictions of the models [14]. Basically, the coefficient of variation was used to measure the residual variation in the data [11].

Model adequacy checking

Model adequacy checking is always necessary to verify the fitted model to ensure that it provides an adequate approximation [13]. Figure 1a displays a normal probability plot of residuals. The plot of these points is reasonably attached close to a straight line, supporting the conclusion that only rPP, RWF, MAPP, and UV stabilizer significantly affect. Likewise, there is no strong indication of nonnormality and possible presence of outliers, which is the very much larger residual than any of the others [11]. The predicted hardness vs. actual hardness is also shown in Figure 1b. It illustrates the linear correlation between the predicted value and observation data, which was well fitted. These correlations verified that the model is adequate to predict the hardness value. From model adequacy checking, the overall predictive capability of model based on the residuals is very satisfactory.

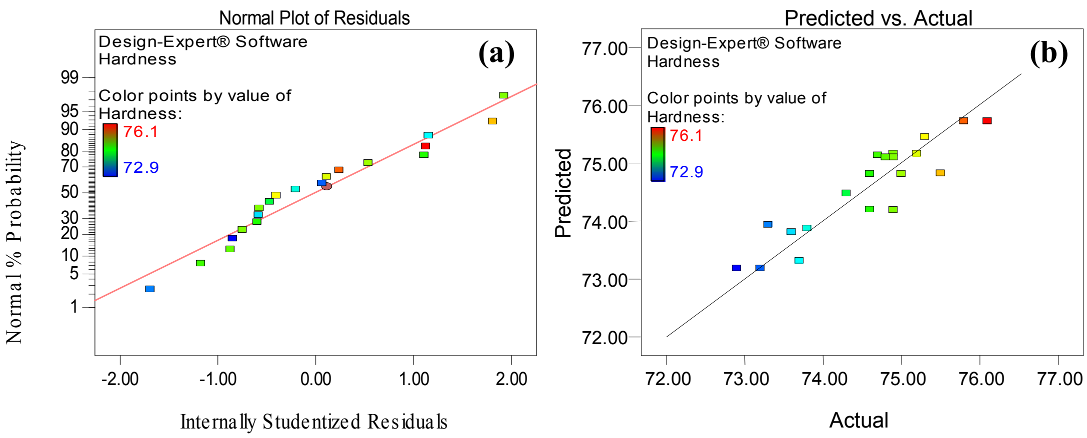

Fig. 1 (a) Normal probability plot of residuals and (b) plot of predicted versus actual hardness.

Effect of compositions on hardness

Significant linear model of the hardness property, affected by the WPC compositions, was obtained from the hardness response. The equation calculated from the regression data was:

$$\text{Hardness} = 73.74x_1 + 75.82x_2 + 75.12x_3 + 62.02x_4 \quad (1)$$

The linear equation of hardness shows positive coefficient of all the compositions, revealing the positive effect on the hardness property. The rubberwood flour (x_2) yielded the highest positive effect as compared with the other compositions. The covered experimental regions of hardness property are shown in Figures 2a and 2b. As seen in Figure 2a, the region is triangular contour plot, in which three compositions (rPP, RWF, and MAPP) were placed at the corners, while the other materials were fixed (UV stabilizer at 0.5 wt% and Lub at 1 wt%). The clear area in triangular contour plot reveals the hardness values varying in range of 73.66 to 75.38 shore D. The hardness value sharply increased with enhancing RWF content but greatly decreased with increase of rPP loading. This is because of higher hardness of rubberwood filler than the weak polymer matrix [3, 7]. In addition, flexibility of the composites was reduced by an increase of RWF content, resulting in more rigid composites [15, 16]. The enhancing addition of MAPP (from 3 wt% to 5 wt%) unaffected the hardness property as shown in the contour plot (Figure 2a). Generally, addition of the coupling agent to the composites increases the hardness with MAPP concentration. This is due to both stronger coupling between the RWF and rPP and better dispersion of the wood flour into the plastic matrix with minimum voids [3, 15, 16]. Furthermore, the effect of UV stabilizer addition is also exhibited in the contour plot (Figure 2b), in which two compositions fixed were the rPP at 59.8 wt% and the Lub at 1 wt%. The area in triangular contour plot presents the hardness values varying in range of 74.2 to 74.8 shore D. The hardness value of rPP/RWF composites slightly reduced with increasing addition of the UV stabilizer. This decrease is attributed due to the negative interaction of mixtures (namely wood flour and UV stabilizer) [3]. In the previous work, Homkhiew et al. [3] found that composites containing 45 wt% RWF and 1 wt% UV stabilizer showed a higher decrease of hardness value than composites with 25 wt% RWF and 1 wt% UV.

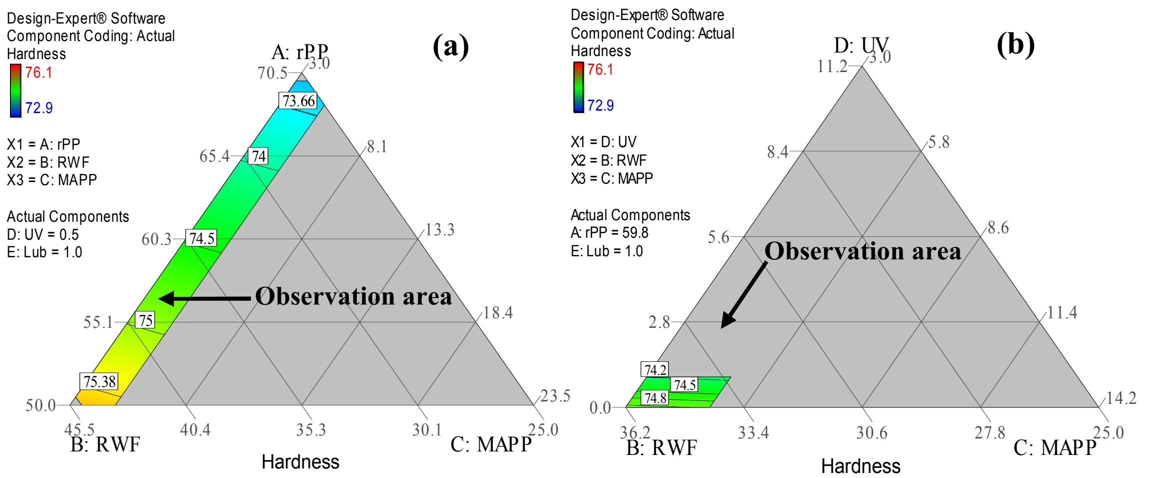

Fig. 2 Triangular contour plots for effects of the compositions on hardness (a) fixed UV stabilizer at 0.5 wt%, Lub at 1 wt% and (b) fixed rPP at 59.8 wt%, Lub at 1 wt%.

Optimal formulation of hardness

An optimal formulation of rPP/RWF composites was conducted to obtain maximum of the hardness value. It was generated by the software, which was produced, analyzed, and presented as a graphical optimization. The optimized point of mixture ratio on desirability and overlay plot is represented in Figures 3a and 3b, respectively. The desirability plot shows a point that maximizes the desirability function to be 0.887, revealing satisfactory value. The desirability level is close to 1, indicating a good hardness response. The obtained desirability exhibited that this point can represent the desired formulation. Likewise, the overlay plot in Figure 3b shows the point of optimal formulation, which is the same point with the desirability plot. The optimal formulation found was 50.0 wt% rPP, 45.0 wt% RWF, 3.9 wt% MAPP, 0.1 wt% UV stabilizer, and 1.0 wt% Lub. Besides, to confirm the accuracy of the model and predicted response, a measurement of the closeness of hardness response obtained from the predicted value and observed result was also validated in Table

3. This result confirmed that the predicted hardness value was not significantly different from the measured value. Concluding that the earlier propose formulation of rPP/RWF composites for the hardness property is reasonable and can be well applied in the WPC industries.

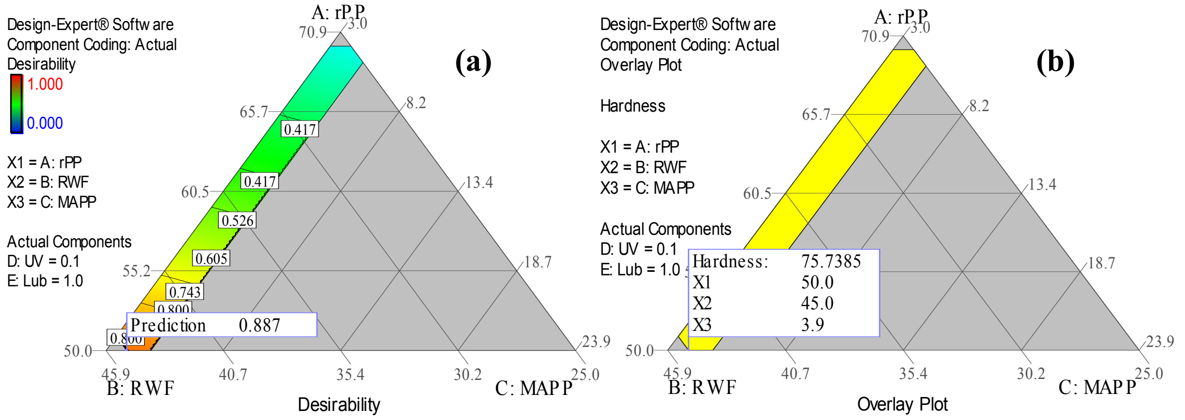

Fig. 3 (a) Desirability plot and (b) overlay plot of hardness for the optimal formulation.

Table 3 Predicted and observed responses with optimized formulation

Mixture component proportion (wt%)					Hardness (Shore D)	
x_1	x_2	x_3	x_4	x_5	Predicted	Observed
50.0	45.0	3.9	0.1	1.0	75.73	75.56 (0.40)*

* The value in parentheses is standard deviation from five replications.

Conclusions

Mixture experimental design, response surface, and optimization methods were applied to determine the optimal formulation based on maximum of the hardness property. Analysis of variance demonstrated that the compositions including rPP, RWF, MAPP, and UV stabilizer significantly affected the hardness property. Model adequacy checking also revealed that the overall predictive capability of model based on the residuals was very strong. From the contour plots, the hardness value sharply enhanced with increasing RWF content but greatly reduced with increase of rPP loading. This is due to the polymer matrix to be a considerably lower hardness than the rigid rubberwood filler [3, 7]. The addition of the UV stabilizer in the composites showed the negative effect, which slightly decreased the hardness value. This result is attributed due to the negative interaction of mixtures [3]. The optimal formulation of rPP/RWF composites using D-optimal mixture design based on maximum hardness value was found to be 50.0 wt% rPP, 45.0 wt% RWF, 3.9 wt% MAPP, 0.1 wt% UV stabilizer, and 1.0 wt% Lub with the desirability function to be 0.887.

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