Photofabrication of Biofiber-Based Polymer Matrix Composites

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Received 19 July 2004; accepted 27 September 2004
DOI 10.1002/app.21402
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The novel development of a photofabrication process of biofiber composites, based on oil palm empty fruit bunch fibers, is reported. The process consists of the following steps: (1) the preparation by a wet process of nonwoven mat of biofiber, either alone or in combination with glass and nylon; (2) drying the mat; (3) preparation of photocurable resin matrix, consisting of vinyl ester and photoinitiator; (4) impregnation of the mat by photocurable resin; and (5) irradiation of the impregnated mat by UV radiation to effect the cure of the composite. The nonwoven mat was formed in a "headbox" into which was poured a slurry of fibers. A wet mat was formed by after dewatering of the slurry. Biofiber, glass, and nylon fibers were mixed in different proportions. A "mixture experimental design" was used to generate experimental compositions of the reinforcing fibers and to model dependency of the response variables on the components through mathematical relationships. These relationships were meant to (1) determine the effect of composition of the reinforcing fibers on the physical and mechanical properties, (2) predict the response for any unknown composition of fibers, and (3) determine the optimum values of any identified properties. Because the product was characterized by multiple responses, simultaneous maximization of all properties was not feasible. The product must be considered in the definition of the trade-off or compromise of properties to obtain overall satisfactory performance. Such an optimization was carried out and the results are reported. J Appl Polym Sci 95: 1493–1499, 2005

Key words: biofibers; composites; photoinitiator; resins; optimization

INTRODUCTION

Recently wood and natural fiber–reinforced composites have gained significant popularity because of the availability of large quantities of biofibers derived from annually renewable resources. Besides strong economic incentives provided by the natural fibers, there are positive environmental benefits gained by such "green" composite materials. These composites are biodegradable and less abrasive so that the life of molding and cutting tools can be prolonged. Since 1998 the market for the biofiber-filled composites has grown more than 25% a year[1] and the prognosis is that it is expected to grow in excess of 14% until 2010. Major application areas are in the building and automobile industries. Biofiber–polymer matrix composites are generally made using thermoplastic or thermosetting resins such as unsaturated polyester, polypropylene, and polyethylene. Sheet molding compounds (SMC), based on unsaturated polyester–oil palm fiber, were developed and reported in earlier publications.[2–4] Uses of sisal, kenaf, jute, hemp, coir, flax, wood, and cellulose fibers in the formulations of SMC have recently been reported.[5] Those composites were processed by application of heat in compression, transfer-molding presses or injection-molding machines. Those processes are both energy and capital intensive, thus necessitating costly equipment and machinery. The room-temperature–curing systems are time consuming and require substantial space.

Recent advances in photochemistry, irradiation equipment, development of photoreactive multifunctional telechelic oligomers and monomers, and advanced photoinitiators have revolutionized the curing technology in the coatings and adhesive industries. Today, technical innovations are bringing the advantages of UV curing to applications requiring the cure of thick composites.

Photopolymerization is the curing process that involves the transformation of liquid or low melting solid oligomers to crosslinked durable products under the influence of ultraviolet radiation. The photochemical UV curing process consists of irradiating a mixture of liquid monomers, oligomers, and a small amount of photoinitiators. The mixture, on exposure to UV light, hardens instantly to become a tough clear product. The final product may be decorative printing inks, adhesives, and polymer matrices in a composite material.

Two options are available for the UV-curable systems: (1) a process induced by free-radical photoini-

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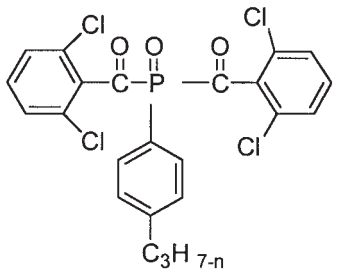
Contract grant sponsor: Universiti Sains Malaysia.

tiator and (2) a process induced by cationic photoinitiators.

The UV-curable systems were initially used for effecting the cure of thin layers of coatings and adhesives. The attenuation of the intensity of UV light as the radiation passes through thick sections limited the use of this technology to cure of thin layers. However, recent development of bisacylphosphine oxide (BAPO), a free-radical type of photoinitiator, or a blend of BAPO and Irgacure 184 (an alpha hydroxy alkylphenone) has opened new opportunities in the field of curing thick pigmented coatings as well as thick sections of glass-fiber–reinforced composite materials. The new photoinitiators exhibit an interesting property known as " photobleaching." This phenomenon is caused as a result of the difference in the absorption characteristics of the photolysis products from those of the original molecule. By virtue of the photobleaching phenomenon the radiation can pass unhindered through the thick sections and enable efficient curing of the submerged layers of coatings and composites. They show excellent properties in through-curing of highly pigmented white lacquers as well as glass-fiber–reinforced materials, several millimeters thick. They also effectively cure thicker coatings that contain colored pigments or even carbon black. Photofabrication of glass-fiber composites is an outcome of the development of this new photoinitiator. Although reports have appeared on the preparation of glass-fiber–based composites, photofabrication of biofiber composites has so far not been reported.

Biofiber-based composites are currently produced by using a thermally curable process. Curing by UV radiation has advantages over the thermal curing process for the following reasons:

1. Curing by UV radiation is ultrafast, so high productivity can be achieved.
2. Because the UV-curable formulations are "single pack" systems with very long "pot life" (in contrast to room-temperature–curable "two pack" systems using methyl ethyl ketone peroxide), no curing of the resin occurs unless they are exposed to UV radiation. The viscosity of the formulations remains unaltered during the application of the resin and impregnation of the mat. The consistency of quality of the product can therefore be ensured. Further, reduction of the wastage of "in-process" resinous materials is also achievable.
3. UV curing is environmentally friendly and saves energy, time, and space.
4. Because of the appropriate choice of UV lamps and photoinitiators, a uniform and consistent "through-cure" can be achieved.
5. The UV curing process eliminates the use of peroxides used in conventional curing systems.



Bisacylphosphine oxide

Scheme 1 Bisacylphosphine oxide.

6. Because the curing reaction goes to near completion, the residual styrene is absent in the cured product, a desirable characteristic not achievable in peroxide-based curing systems.

This article reports on the development of a process for photofabrication of biofiber composites based on oil palm empty fruit bunch fiber. Ultraviolet radiation was used for effecting the cure of the composites. Glass and nylon fibers were also incorporated in different quantities. A "mixture" experimental design was used to generate experimental compositions of the reinforcing fibers and to model the dependency of the response variables on the components through mathematical relationships. These relationships were meant (1) to determine the effect of the composition of the reinforcing fibers, both singly as well as in combinations, on the physical and mechanical properties; (2) to predict the response for any combination of components; and (3) to determine the optimal values of any identified properties.

Brominated vinyl ester was used as matrix material. Bisacyl phosphine oxide was used as the photoinitiator.

EXPERIMENTAL

Materials

Oil palm empty fruit bunch (OPEFB) was obtained from Sebutek Sdn Bhd (Kuala Lumpur, Malaysia). The epoxy vinyl ester Derakane 510 (an unsaturated polyester resin) was obtained from Euro-Pharma Sdn Bhd (Kuala Lumpur, Malaysia). The photoinitiator Irgacure 1800 (a bisacylphosphine oxide; see Scheme 1) was supplied by Ciba Specialty Ltd. (Singapore). Table I.

Methods

Design of experiments

To evaluate the performance of the composites and optimize the reinforcement compositions, a "mixture experimental design" [6–9] was adopted to (1) determine the compositions of the fibers for various exper-

iments, (2) develop statistical models that quantify the effect of compositional variables on the product performance, (3) identify the interaction of factors that affect the product, and (4) interpret the results using response surface methodology and optimization technique.

In contrast to the response surface methodologies involving process variables, where the levels of each factor are independent of the levels of other factors, in mixture experiments the factors constitute components or ingredients of a mixture and, consequently, their levels are not independent and are subject to the following constraint[6]:

$$0 \leq x_i \leq 1 \quad i = 1, 2, 3, \ldots, p$$

where $x_1 + x_2 + x_3 + \cdots + x_p = 1$ (i.e., 100%).

For a three-component mixture used in the present work, the mixture space is a triangle with the vertices corresponding to formulations that contain "pure blends" (100% of a single component). The constrained experimental region is conveniently represented on trilinear coordinate paper, as shown in Figures 1 to 6. "Simplex designs" are used to study the effect of mixture composition on the response variable. To accommodate a polynomial equation to represent the response surface over the simplex region, the natural choice of an experimental design[8] is the one whose points are spread evenly over the whole simplex factor space. An ordered arrangement, consisting of uniformly spaced distribution of points, is known as a "lattice." However, such a lattice has a special correspondence to a specific polynomial equation. For example, to support a polynomial model of degree m in q components over the simplex, the lattice, referred to as $\{q, m\}$ simplex lattice consists of points whose coordinates are defined by the following combination of component proportions[8]:

$$x_i = 0, 1/m, 2/m, 3/m \ldots 1$$

As an illustration, let $p = 3$ and $m = 2$. Then $x_i = 0, \frac{1}{2}, 1$ $(i = 1, 2, 3)$ and the simplex lattice consists of the following six runs: (1, 0, 0), (0, 1, 0), (0, 0, 1), $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, 0, \frac{1}{2})$.

A new type of mixture design called D-optimal point selection has been recommended by Myers and Montgomery[7] and is included in the Design Expert software, which was used in the present investigation. The D-optimal design is said to minimize the general variance of the coefficients in the polynomial models, the "canonical polynomials" given in Table I. This design was adopted in the present work to collect the experimental data. The D-optimal points were augmented to provide for estimates of pure error by replication, and to determine the lack of fit using excess design points.

An appropriate choice of functional relationships was made from among the "canonical polynomials" (Table I). The Design Expert software also made possible the graphical representation of the data and optimization.

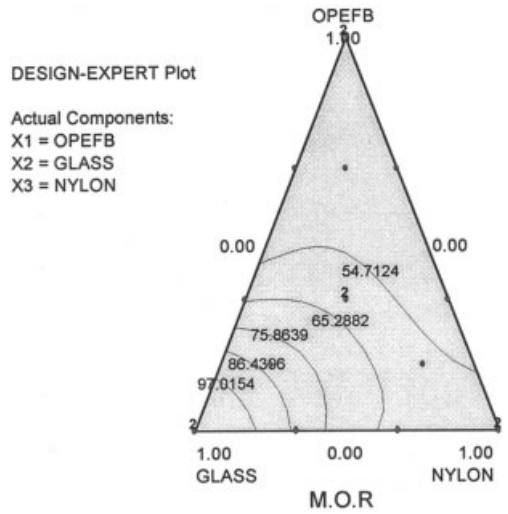


Figure 1 Effect of fiber composition on modulus of rupture (MOR) (contour plots).

TABLE I
Canonical Polynomials

Type	Equation
Linear	$E(Y) = \sum_{i=1}^{q} \beta_i x_i$
Quadratic	$E(Y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \sum_{i<j}^{q} \beta_{ij} x_i x_j$
Cubic	$E(Y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \sum_{i<j}^{q} \beta_{ij} x_i x_j + \sum_{j=1}^{q} \sum_{i<j}^{q} \delta_{ij} x_i x_j (x_i - x_j) + \sum_{k=1}^{q} \sum_{j<k}^{q} \sum_{i<j}^{q} \beta_{ijk} x_i x_j x_k$
Special Cubic	$E(Y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \sum_{i<j}^{q} \beta_{ij} x_i x_j + \sum_{k=1}^{q} \sum_{j<k}^{q} \sum_{i<j}^{q} \beta_{ijk} x_i x_j x_k$

TABLE II
Experimental Data

Run	Factor A: OPEFB	Factor B: Glass	Factor C: Nylon	Density (g/cm^3)	Water absorption (%)	Impact strength kJ/m^2	Tensile strength N/mm^2	MOR (N/mm^2)	Gel content (%)
1	0.00	0.00	1.00	1.09	1.36	11.21	27.3	60.62	100
2	1.00	0.00	0.00	1.15	2.36	4.4	18.42	47.15	100
3	0.00	0.00	1.00	1.08	1.59	13.3	22.2	63.4	99
4	0.00	0.67	0.33	1.18	0.89	17.1	48.3	70.9	100
5	0.67	0.33	0.00	1.12	2.49	8.7	29.7	42.85	97
6	0.00	1.00	0.00	1.24	0.95	18.14	37.63	108.95	100
7	0.33	0.33	0.33	1.18	2.05	13.4	25.8	55	96
8	0.67	0.17	0.17	1.12	2.62	12.2	21.25	52.37	95
9	0.67	0.00	0.33	1.14	2.43	7.8	13.73	41.47	99
10	0.33	0.00	0.67	1.13	1.77	17.54	24.2	58.41	97
11	0.17	0.17	0.67	1.16	1.54	15.77	25.91	63.14	97.6
12	0.33	0.33	0.33	1.15	1.62	9.02	25.74	57.93	97.56
13	0.00	1.00	0.00	1.24	1.11	17.97	59.8	104.5	100
14	1.00	0.00	0.00	1.15	2.59	5.83	17.51	47.19	98
15	0.17	0.67	0.17	1.2	1.51	14.4	36.3	89.8	97.6
16	0.33	0.67	0.00	1.21	1.73	8.15	33.83	73.47	100
17	0.00	0.33	0.67	1.14	1.31	12.82	30.4	74.66	99

The experimental compositions of the fiber reinforcements, based on the D-optimal design, are shown in Table II together with the results on the physical and mechanical properties of the photofabricated composites derived therefrom.

Process of making biofiber composite

Preparation of the matrix resin. Irgacure 1800 (3% by weight) was added to the vinyl ester resin and stirred thoroughly at room temperature for about 15 min.

Preparation of the nonwoven reinforcing fiber mat. A simple technique was developed by using the "head-box" or "deckle-box" principle to prepare the nonwoven mat of biofiber or hybrid fibers. This simple method replaces expensive machines used to prepare nonwoven mats and can be adopted in any laboratory or small-scale industrial operation. The palm fibers were cut to a length of about 2.5 cm. Similarly, glass-fiber and nylon fibers were cut to the same size. The composition of the fiber mixture was varied in accordance with the statistical experimental procedure described under "Mixture Design." The actual compositions were computer generated. Once the compositions were fixed, the appropriate weight of the individual fibers was dispersed in water. A consistency of about 3% was found suitable for the formation of the reinforcing mat. The slurry was stirred well to ensure a uniform distribution, after which it was poured into a "deckle box," which consisted of a vertical rectangular vessel made of Perspex. At the bottom of the vessel was positioned a sieve made of nylon. A wooden frame surrounded the sieve and kept the sieve in position. After the slurry was poured into the deckle box, dewatering occurred through the sieve, leaving the fiber wet mat on the sieve. The wet mat was carefully removed from the sieve and transferred to a tray. The tray was kept in an oven maintained at about 110°C until the moisture content was about 3%. The dry mat was supported on a polyethylene film. In the meanwhile the "matrix resin" was prepared separately.

Impregnation of mat with the resin. The dry hybrid OPEFB–nylon–glass-fiber mat, as prepared by the procedure mentioned above, was placed on a polyester film and the resin containing the photoinitiator was poured uniformly onto the surface of the mat. A second polyester film was placed on the mat and the resin impregnation was achieved by squeezing the mat by means of rollers to eliminate air bubbles.

UV irradiation of the impregnated mat. The impregnated assembly was then placed on a conveyor belt and passed through the UV irradiator. On exposure to the UV radiation, the matrix resin underwent polymerization and the material was transformed into a thermoset composite. It required about 10 to 15 passes at a conveyor speed of 15 m/min (about 1 min or less exposure time) for a complete cure of the composite. After the cure, the frames were carefully removed. The polyester films were removed from the cured composite.

Determination of physical and mechanical properties of the composites. The following physical and mechanical properties of the composites were determined by the methods defined in various ASTM standards. The mechanical tests were carried out using a Universal testing machine (Model STM-10, Zwick, Bamberg, Germany) at a crosshead speed of 1 mm/min according to ASTM D 3039. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined by three-point bending according to ASTM D 790. Tensile strength was determined by ASTM D 3039-76. The

Izod Impact test was carried out according to ASTM D 256-81. The percentage of curing was determined by the gel content according to ASTM D 2765. Water absorption was determined by ASTM D 570.

RESULTS AND DISCUSSION

The results on the effect of compositional variables on the physical and mechanical properties are tabulated in Table II. The results were analyzed using Design Expert® software. The data were fitted to Scheffé-type mixture models. The coefficients of the models and the variances of the model coefficient estimates were computed from the software.

Generally, as one would expect, the mechanical properties of the hybrid composites were improved by an increase in glass-fiber content. However, the objective of the present investigation was to optimize the composition of the overall reinforcement to produce any desired compromise between the strength and the cost. This was achieved by establishing the mathematical relationships between the compositional variables and the various strength properties and representing the results as three-dimensional response surfaces, as contour plots or as trace plots (Figs. 1–8). Trace plots provide "silhouette" views of the response surface.[7,9] The response trace plots show the effects of changing each component along an imaginary line from the reference blend defaulted at the overall centroid. The desired region in the "simplex" (triangular diagrams) can be chosen and the conditions to produce any desired response can easily be determined.

The Design Expert software also contains computing features by which suitable composition of the reinforcement can be determined for any desired combination of strength values under various prescribed constraints with respect to the composition of reinforcement. These results are discussed below.

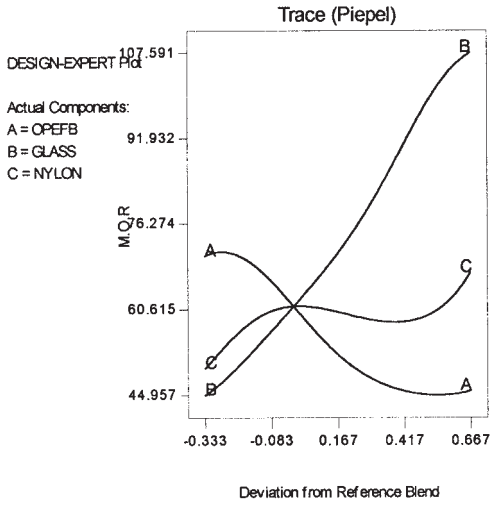


Figure 2 Effect of fiber composition on MOR (trace plots).

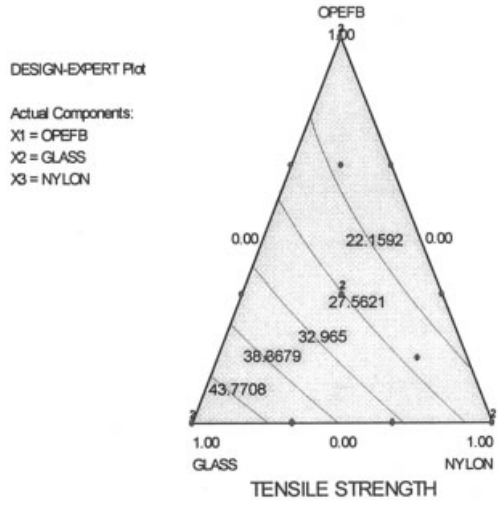


Figure 3 Effect of fiber composition on tensile strength (contour plots).

Effect of compositional variables on the modulus of rupture (MOR)

The experimental results were found to fit ($p = 0.0006$ or $F = 11.46$) the following special cubic function with "Logit" transformation defined by

$$y' = \ln \{(y - \text{lower})/(\text{Upper} - y)\}$$

with a correlation coefficient R^2 of 0.8731 and an insignificant lack of fit ($p = 0.1787$).

The above relationship is shown graphically as contours in Figure 1 and as trace plots in Figure 2. It can be seen that the MOR of the composite increased with increasing percentage of glass and decreased as the biofiber content increased. The increase in the percentage of nylon fiber does not significantly affect the MOR.

Effect of compositional variables on the tensile strength

Again, a special cubic function can adequately describe the experimental results with a high significance ($p = 0.0009$) and an insignificant lack of fit ($p = 0.9356$). The correlation coefficient (R^2 value = 0.82) was also high. Figures 3 and 4 depict the results as contour plots and trace plots, respectively. As in the case of MOR, the tensile strength also showed a similar trend. As the glass-fiber content increased, the tensile strength increased, as expected. Biofiber decreased the tensile strength, as one would expect. On the other hand, the tensile strength remained unimpaired by changes in the nylon content.

Effect of compositional variables on impact strength

A special cubic function with a significant probability value ($p = 0.0032$), insignificant lack of fit ($p = 0.1890$),

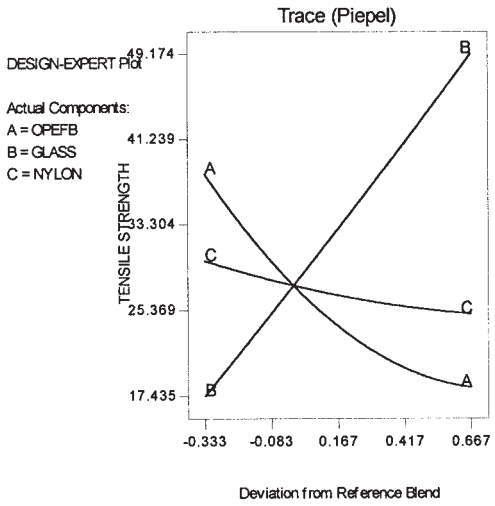


Figure 4 Effect of fiber composition on tensile strength (trace plots).

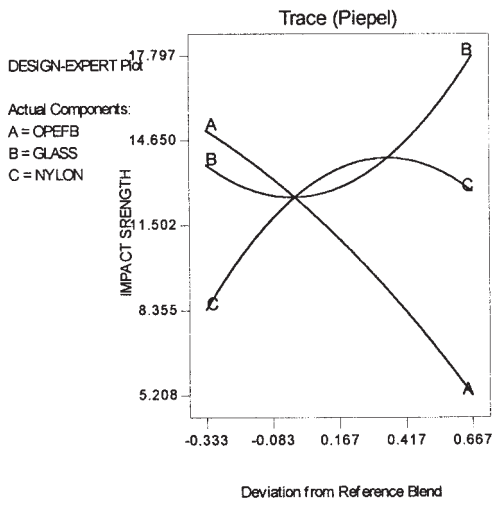


Figure 6 Effect of fiber composition on impact strength (trace plots).

and reasonable correlation coefficient ($R^2 = 0.766$) was found to adequately describe the experimental data on the impact strength values. The data are represented as contour plots in Figure 5 and as trace plots in Figure 6.

Whereas the increase in the percentage of organic fiber decreased the impact strength, both glass fiber and nylon fiber increased the impact strength.

Effect of compositional variables on the water absorption

The water absorption of photofabricated composites was correlated with the fiber composition, through a linear relationship, with a very good significance ($p = 0.0001$), insignificant lack of fit ($p = 0.4136$), and a high correlation coefficient ($R^2 = 0.867$). The above mathematical relationship is shown as contour plots and trace plots in Figures 7 and 8, respectively. It can be seen that the glass fiber and the nylon fiber decreased the water absorption, whereas the biofibers increased the water absorption. However, the overall water absorption values of the composites under any condition were quite low.

Effect of compositional variables on the gel content

Table I shows that the gel content values, as determined by toluene extraction in a Soxhlet apparatus, were very high (nearing 100%) under all conditions. Therefore it can be concluded that the curing of the matrix material by the UV radiation was not adversely affected by any organic component present in the biofiber and thus no expensive pretreatment of the fibers was necessary.

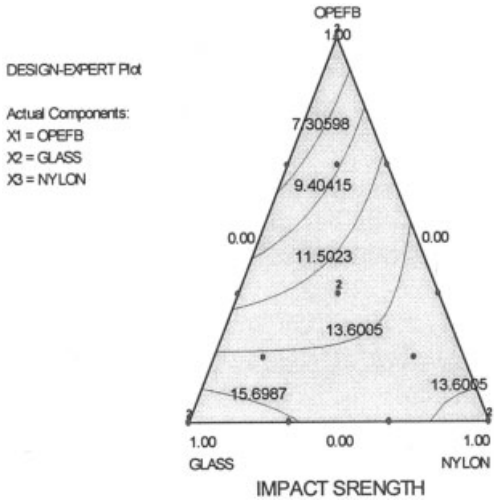


Figure 5 Effect of fiber composition on impact strength (contour plots).

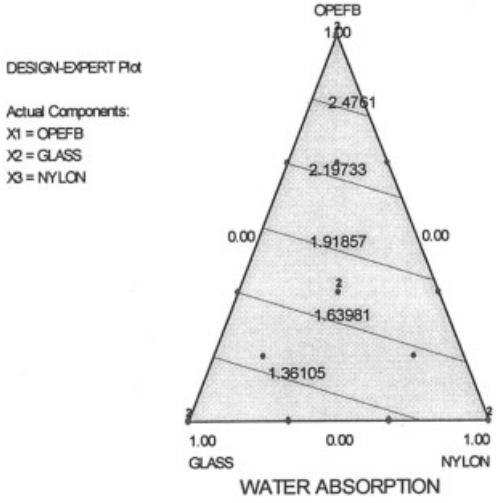


Figure 7 Effect of fiber composition on water absorption (contour plots).

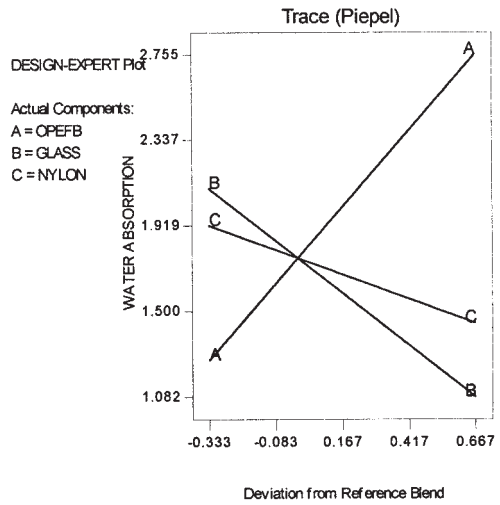


Figure 8 Effect of fiber composition on water absorption (trace plots).

Optimization of the fiber composition

In the present investigation there were multiple responses: modulus of rupture, impact strength, tensile strength, and water absorption. It was not possible to maximize all these responses simultaneously and it may necessitate compromise or "trade off" of some properties so that the overall performance is satisfactory. There have been many creative approaches put forth in the statistics literature for the analysis of multiple responses. Many times a simple overlaying of contour plots will enlighten researchers and a reasonable compromise becomes obvious, suggesting a desirable region of optimum overall performance, although the contour overlay methodology can become unruly. Derringer and Suich[10] developed an interesting procedure that can be useful when several responses are involved. Their method makes use of a desirability function in which the researchers' own priorities and desires on the response values are built into the optimization procedure. This method is described in detail by Myers and Montgomery.[7] The Design Expert software provides the facility for carrying out optimization of multiple responses and can be performed graphically or numerically.

In the present investigation it was desired to optimize the process of making the composite with maximum incorporation of biofiber under the constraint that the percentages of glass fiber and nylon are in the range 0.15 to 0.35.

The computer solution for the optimum composition of the fibers (in weight fractions) was: 0.41 OPEFB, 0.35 glass, and 0.24 nylon.

The resulting composite would have an impact strength of 11.56 kJ/mm^2, a tensile strength of 29.021 N/mm^2, and a modulus of rupture of 61.1 N/mm^2.

Similar optimizations can be performed for any desired combination of responses and for any desired specification of fiber composition.

CONCLUSIONS

Photofabrication of composites was produced from hybrid reinforcement, consisting of oil palm empty fruit bunch fibers, nylon fiber, and glass fiber. The hybrid nonwoven mat was made by a simple wet process using "head box" or "deckle box." Impregnation with photocurable resin and subsequent exposure to ultraviolet radiation resulted in an ultrafast curing of the composites. "Mixture design" was used for collecting and analyzing the data and optimization of the process. Physical and mechanical properties were determined by standard methods. Appropriate mathematical models were obtained from the experimental data and the models were validated using Design Expert software. Because the product was characterized by multiple responses (properties), simultaneous maximization of all properties could not be achieved and a "trade-off" or compromise was needed to obtain an overall acceptable performance. Design Expert software enabled such an optimization to be performed.

The authors acknowledge with thanks the Universiti Sains Malalaysia for the financial assistance under a short-term grant.

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