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An assessment of the water absorption properties of an orange peel particulate-based epoxy composite by optimisation

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Abstract

Biocomposites are numerous and of increasing use in a wide range of composite applications in recent years. To achieve an overall low life-cycle cost, water absorption characteristics are of significant interest. Despite the availability of numerous water absorption studies on green fillers, investigations with particular focus on orange peel particulate (OPP) composites are still missing from the literature. An experiment was conducted to measure and optimise the water absorption behaviour of an OPP epoxy composite using the Taguchi method. Microstructural examination of the water-absorbed specimens was done after several days of immersion using scanning electron microscopy. This was done to understand the water absorption mechanism and analyse both water-eroded surfaces as well as the eroded debris using SEM morphological analysis. Results showed that a 5% OPPs composite showed greater water absorption than a pure epoxy sample across all the periodic readings. This was due to the presence of orange peel particles in the composites. The Taguchi method obtained optimal parametric setting of $A_1B_1C_1$ for both materials, which corresponds to low water absorption values for the pure epoxy and 5% OPPs composite. The final masses of pure epoxy and 5% OPPs composite were found to have the highest percentage contribution to the water absorption optimisation using analysis of variance (ANOVA). Furthermore, application of the Pareto 80-20 rule to the Taguchi optimisation yielded results in agreement with the ANOVA at a high level of significance regarding water absorption properties.

Keywords: Water absorption, Taguchi method, Epoxy, Composite, Pareto

1. Introduction

Biocomposites [1-5] have emerged over the past few years as a principal challenger to non-natural particulate or fibre-based composite materials over a broad spectrum. The quest for novel materials with attractive properties for sporting facilities, household interior decorations and designer materials has prompted the design and development of more appealing, useful and less-costly polymer composites [6]. Composites have outstanding and unattainable characteristics in comparison with monolithic materials. They are distinctly built such that the most striking features and characteristics of their constituents are displayed while their worst and most undesirable characteristics are suppressed [3, 5-6]. This makes development of novel composites one of the most active areas of engineering and science today.

Natural particulates are of tremendous utility for low-weight composites. Environmental issues and economic concerns are also fundamental in the choice of fillers. Studies have been based on the use of fillers such as cotton fabrics [3], sisal-coconut coir combination [7], sisal [2, 8], wood flour [9], hemp [10-13], sisal and jute combinations [14], jute [6, 15], kenaf [16] and flax [17]. In the present day research on natural particulate polymer composites, environmental issues appear as a top agenda item in global studies on composites. Consequently, significant investigations of various fabrication techniques as well as a wide array of scientific properties of polymer composites with various fillers have been done.

There is a vast scientific body of knowledge on water absorption of polymer composites. Studies include comparison of water absorption tendencies of composites in treated and untreated modes [3, 6, 18]. Substantial evidence from the water absorption literature shows that the higher moisture absorption potential of natural cellulosic fibres is the principal shortcoming of polymer based composites. This problem leads to the developments of micro-cracks, yielding reduced strength threshold values of some composites and has long-term performance effects on their mechanical properties. Stress arises in a naturalfibre as well as the matrix of a composite as a result of moisture absorption over the long-term. Therefore, chemical treatment is fundamental to solving this problem [19].

Kim and Seo [8] reported a significant effect of the water absorption on the mechanical properties of a sisal textile reinforced epoxy composite (see also [20]). Costa and D'Almaida [14] varied the stress as well as the elastic

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modulus as composites aged in distilled water. A jute-epoxy composite emerged with the most favoured properties for all of the immersion times. Dhakal et al. [11] demonstrated the influence of water absorption on the mechanical properties of hemp-based composite (see also [21]) using the fibre's volume fraction. It was concluded that an increase in weight gain corresponded to the increased volume fraction of the composite. Tensile as well as flexural properties of the composite declined when the weight-gain increased.

Kord [9] studied the influence of wood flour quantity on the hardness as well as the water uptake of a polypropylene composite. It was concluded that the hardness of the composite increased with quantity of the wood flour used. Masoodi and Pillai [15] studied the weight-gain characteristics of a jute fibre epoxy composite. It was concluded that the rate of moisture diffusion into the composite increased with the ratio of jute-fibre-to-epoxy.

Girisha et al. [7] experimented with sisal/coir/epoxy hybrid composite specimens and observed a decline in tensile flexural properties as the moisture uptake increased. Chen et al. [10] studied the influence of isocyanatoethyl methacrylate treatment on the water absorption of a hemp/unsaturated polyester composite. They reported a substantial increase in the resistance to water for these specimens. By studying cotton fabric/geopolymer composite, Alomayri et al. [3] noted a decline in the mechanical behaviour of a composite due to water absorption. Huner [17] tested the behaviour of a flax fibre in terms of moisture absorption and noted that the mechanical properties decreased with increasing moisture content.

Natural filler based composites have tremendous advantages. Notable among these benefits are that they are renewable and biodegradable resources, thus mitigate environmental pollution and contamination. They also have lower costs in life-cycle analysis, lighterweight and attractive mechanical properties. Unfortunately, they are hygroscopic and under some environmental conditions, and this negatively impacts their use at high levels composite developmental work [6]. Cellulosic materials incorporated into natural particulates are the principal water absorption elements [18]. The process of water absorption in these materials is related to the hydroxyl groups present in the material. They increase the hydrophilic nature of the composites. Thus, the hydrogen bonding of the molecules of water to the hydroxyl groups within the cell walls gives rise to water absorption [6]. The result is an accumulation of moisture within cell walls and particulate swelling. This also takes place in the particulate-matrix interface [6]. The overall result is a drastic dimensional instability of the cellulosic composites. Linear expansion caused by the reversible and irreversible actions affects these composites [6, 19].

Although many important deductions can be made from earlier studies on water absorption of other wastes such as cotton fabric, jute, sisal and hemp, it is difficult to directly relate these to orange peel particulate-based applications. It is notable that orange peels contain some oily materials, which may affect the water absorption of any material containing them. So, literature values of other wastes have limited use for manufacturing decisions involving OPPs epoxy composites. The problems faced when using natural particulate filler-based composites are compounded with a decrease in the adhesive strength between the particulate and the matrix. This leads to deterioration of the composite's mechanical properties [1, 6]. It has been observed that many composites that contain cellulose and are used in outdoor applications are most often exposed to humid conditions during their lifespan. Orange peels are increasingly attractive from the perspective of their use in green product development and reduced costs. In many real life applications in which composites are used, the trend is towards the use of lightweight materials and fillers that reduce the overall weight of the material. OPPs satisfy this requirement and are potentially very attractive to designers and fabricators. OPP is light and will reduce the overall weight of a composite in which it is used. This weight reduction is significant, having implications for cost in terms of fuel efficiency for engines utilising them as a composite-based engine compartment. Additionally, orange peels have some oily secretions that can impart some water resistance. Presently, there is a paucity of research on the water absorption characteristics of composites reinforced with orange peel particulates. However, developing more complete knowledge of the hygroscopic characteristics of orange peel particulate epoxy composites is fundamental to their use in various environments exposed to the weather, as well as to enhance their long-term performance [22-24]. Very little technical information is available from the literature regarding water absorption of particulate based biowastes. Prior studies dealt with fibers. Additionally, locally available orange peel waste based composites in Nigeria and other developing countries have not been reported in the literature. Hence, addressing this vital issue in a systematic value adding manner is essential for the expansion of the literature on composite materials.

Orange peel based epoxy composite testing has been restricted to mechanical testing and impact testing. When the fibre or orange peels was used for reinforcement, 0.600 mm sized particulates were not discussed. Reports of absorption tests for OPPs composites have not been made. Some research has been done to examine the water absorption behaviour of OPP composites [25] at ambient temperatures and humidity. This was done to improve the stress transfer between the particulates and matrix [26]. Demonstration of improved resistance to water absorption with OPPs is important. It remains a pivotal effort among competing composite manufacturers.Transferring this knowledge to the industry for improved composite performance has important industrial implications [27]. From this viewpoint, the industry would derive major benefits from this research.

2. Experimental

2.1. Experimental materials

The principal materials utilised in this work are orange peel particle, epoxy resin and the amine hardener. Orange peel particles (OPP) were prepared by sun drying freshly collected orange peels in cut open polyethylene bags to remove moisture. Complete dryness was attained when the colouration of the peels changed from greenish-yellow to brownish-black. This was also accompanied by crispiness and shape change of the peels. The dried orange peels were pulverized in local grinding mills with the use of a diesel powered engine (SWSST, Germany) for 12 complete passes until fine particles was achieved. The particulate orange peels were sieved with the aid of a British standard sieve (ELE International Laboratory Test Sieve) in an electric powered shaker (Impact Auto Sieve Shaker). This was done for an average of 20 minutes for every run using a size range of 75-600 µ (0.075-0.600 mm). Only the 75 µ orange peel particles were used in this work. Protective covering and gloves wereworn to mitigate the effect of static electricity.

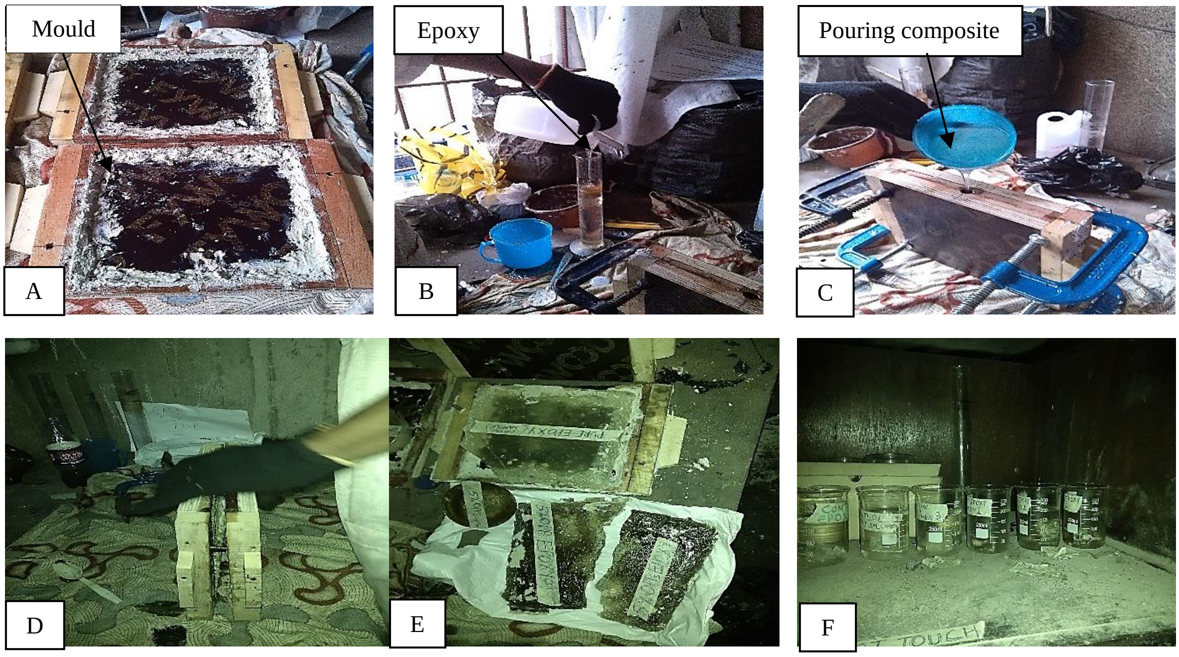


Figure 1 A - Preparation of the mould for casting; B – Measuring epoxy in a cylinder before mixing with orange peel particles; C – Pouring mixed epoxy and orange peel particulate into a prepared mould; D – Dismantling the cured epoxy composite after 24 hours; E – Solidified epoxy composites; F – OPP-epoxy composite in water

Epoxy resin (LY 556) and Amine hardener, both manufactured by Blue Sea Resin Industries, Limited (No. 85, Beiyuan Street, West District, Chiayi City, Taiwan, Republic of China) were purchased through Tony Nigeria Enterprises, a chemical marketing and retailing shop based in Ojota, Lagos, Nigeria.

2.2 Experimental procedure

In this investigation, a gelatinous state approach of creating composite material was employed in which the orange peel particles, the dispersed phase was hand mixed with the epoxy resin through physical stirring. A 5 wt% (parts per hundred of total polymer) of orange peel particles was prepared for addition to epoxy resin matrix in the ratio 1:0.05. Epoxy resin and amine hardener were combined in the ratio 1:0.5 by weight in a heat-resistant container until a homogenous mixture was formed. The measured quantity of orange peel particles was added to the epoxy matrix. The composition was hand mixed thoroughly for 5 minutes to avoid trapping air bubbles that could lead to the formation of voids and gaps. The gelatinous material was carefully poured at the onset of the exothermic reaction between epoxy and hardener into a prepared wooden mould (Figure 1). This was done to avoid the material being cured (solidifying) outside the mould, which could lead to inconsistency in structure and morphology. The inward part of the mould was coated with bulk engine oil purchased from Total Nigeria filling station for ease of removal of the composite from the mould. Ambient temperature and conditions was assumed for the mould used in this experiment. Wood, which the mould is made of, is not a good conductor of heat and can assume the ambient temperature irrespective of reactions taking place. This is unlike in steel or aluminiummoulds, which can conserve heat for longer periods of time. Therefore, the epoxy/hardener combination used in this work can cure evenly and quickly under ambient conditions without the influence of mould temperature. A newly fabricated mouldwas used in this work, and this was done to avoid dimensional inaccuracies to fabricated composites susceptible to aged moulds.

In this paper, the FTIR analysis was conducted on the organic material, epoxy. This was motivated by the need to recognise the chemical compounds in the epoxy used in an extensive array of competence. The acronym FTIR signifies Fourier Transform InfraRed, which is a favoured technique of infrared spectroscopy. An important attribute of this technique is that IR radiation is set to traverse a specimen. In the process, certain portions are absorbed by the specimen while the remaining portions are transmitted. The outcome spectrum corresponds to molecular absorption as well as transmission, producing a sample's fingerprint. The unique attribute is that no two distinctive structures are competent to create the same infrared spectrum. FTIR offers a prompt and revealing route in chemical analysis.

To illustrate the Holtz and Gibbs' free swell concept [28-29], it is noteworthy to state that the phenomenon of free swell, which has been for ages applied to check the expansivity of soils when used in water-based applications has now graduated to applications in composite manufacture. The foundation of the phenomenon is that the swelling of particles (i.e. soils and particulate orange peels) can be attributed to a reduction in the effective stress acting on the bulk sample such that the total repulsive pressure draws apart the intermingles particles. In other words, when a partially saturated sample with minimal water content passes through water, pore pressure increases while the effective stress is reduced which makes swelling to occur.

In this paper, the scanning electron microscope (SEM), which is the main equipment used in scanning electron microscopy has been employed in tests concerning this work and a brief introduction is given here. The SEM is used basically used to produce images from a material after scanning its surface by concentration of a beam of electrons. The image is formed in an unusual way and it differs greatly from that produced by human experience by light as viewed by the eye. There is an interaction that takes place between the focused electrons and the atoms in the sample, which provides signals that reveals the topography and composition of the sample. The SEM equipment comprises of two main components, the electron console and electron column. The discussion here is restricted to the electron column of the SEM equipment. The electron column is where the electron beam is generated before it is concentrated into a small diameter and scanned over the surface of a sample through electromagnetic deflection coils. The key components of the electron column and their functions are described briefly:

1. Electrogun: It is located at the top of the column where free electrons are produced by thermionic emission from a tungsten filament at approximately 2700 K. The electrons are driven towards an adjustable anode between 300 V to 30 kV.
2. Condenser lens: The role of the condenser lenses are to converge the beam and make it pass through a focal point. This reduces it to 1000 times its original size. Therefore, the condenser lenses use the accelerating voltage to determine the intensity of the electron beam when it strikes a sample.
3. Apertures: The work of the aperture is to minimize and remove irrelevant electrons in the lenses. The final lens aperture beneath the scanning coils determines the size of the beam as it hits the specimen. The size will in turn determine the resolution and depth of the field. Reducing the size will increase the resolution and depth of the field with a loss in brightness [30].
4. Scanning system: The electron beam is usually focused on the sample with the aid of deflection coils inside the objective lens. As a result, the electron beam becomes elliptical in shape. The stigmator acts to mitigate this effect by changing it back to circular cross section [30-31].
5. Specimen chamber: The specimen stage and controls are positioned at the lower portion of column. The secondary electrons from the specimen are attached to the detector by a positive charge.

After a good exposure to training and techniques in using the SEM, anybody is expected to be able to produce relatively good images. However, obtaining satisfactory images may become more complicated due to wide range of materials, specific requirement and different scenarios. Some of the factors that should be carefully considered according to technical needs of sample and equipment are image disturbances, effect of accelerating voltage, effect of working distance and effect of spot size.

2.3 Taguchi method and analysis of variance (ANOVA)

The Taguchi method was used to find the optimal setting of parameters that will have minimal uptake of water in the composites. The optimisation process was carried out by organizing the three parameters into factors and levels using the system design. In the Taguchi method, control factors are factors which can be managed under normal production conditions. On the other hand, noise factors are either cumbersome or uneconomical to manage under normal production conditions, while signal factors are those which influence the average performance of the system. The parametric design was used to identify the factor levels that give the desired optimal performance of the system. This entails choosing an appropriate orthogonal array with *Minitab* 16 statistical software package. In this work, initial mass, final mass and weight gain are the factors while their conditions during the water absorption process are taken as the levels. For a 3 factor, 3 level optimisation problem, an L_9 orthogonal array was picked. The orthogonal array distributes all the different factor levels, thereby making it possible to have every possible combination in a virtual experiment. The Taguchi method tests all the various factors and respective levels unlike other optimisation methods that tests one factor at a time. The Microsoft Excel spreadsheet was used in running the Taguchi experiment. The outcome of the experimental trials is expressed as signal-to-noise (S/N) ratio, which is a logarithmic expression of the target quality characteristic.

Table 1 Parameters and levels for the water absorption experiment

Pure Epoxy			
Levels	**Parameters**		
	Initial mass, M_i (g)	**Final mass, M_f (g)**	**Weight gain,* W_g (g)**
1	15.12	18.28	0.55
2	18.47	18.61	0.88
3	19.6	18.59	0.86
5 % OPPs reinforced composite			
1	16.88	19.13	1.17
2	18.12	19.51	1.55
3	18.86	19.53	1.58

* The differences are not the exact substractions because We bifurcated the average values from the experimental data before we applied them as factor levels in the Taguchi experimental design.

Table 2 Taguchi's L_9 orthogonal array

Trial no.	*A*	*B*	*C*
1 (3 days)	1	1	1
2 (5 days)	1	2	2
3 (11 days)	1	3	3
4 (14 days)	2	1	2
5 (20 days)	2	2	3
6 (24 days)	2	3	1
7 (26 days)	3	1	3
8 (31 days)	3	2	1
9 (38 days)	3	3	2

To do optimisation, the three parameters were organised into three levels as shown in Table 1. Therefore, the Taguchi method uses an L_9 orthogonal array having 9 rows, which is equivalent to the number of virtual experiments to be carried out in the study. Table 2 describes the L_9 orthogonal array for the Taguchi experiment. In the control of the levels of each parameter, a number of possibilities exist. Consider the three parameters, initial mass, final mass and weight gain. The initial mass could be varied over a wide range of values. However, the final mass largely depends on the value of the initial mass and also the weight gain. However, if two fillers were used in fabrication of the composite, then the variations of the initial mass would be largely practicable.

From the parameters and levels given in Table 1, the free swell of the samples was calculated using the Holtz and Gibbs' model as follows:

$$\text{Free swell (\%)} = \frac{M_f - M_i}{M_i} \times 100 \quad (1)$$

whereM_f and M_i are the final and initial masses of each sample, respectively, while the quantity $M_f - M_i$ is the weight gained by the sample.

Table 3 Experimental results for free swell and S/N ratios

Experimental trial	Pure epoxy		5 % OPPs composite	
	Free swell	**S/N ratio**	**Free swell**	**S/N ratio**
1 (3 days)	2.479102	-22.719943	4.45231	-23.348707
2 (5 days)	2.206937	-22.801555	5.621245	-23.471127
3 (11 days)	3.753483	-22.842677	8.011464	-23.473866
4 (14 days)	4.014198	-23.515916	8.002266	-23.637546
5 (20 days)	4.683651	-23.583203	8.841137	-23.745021
6 (24 days)	4.798261	-23.612325	8.80307	-23.739846
7 (26 days)	5.253558	-23.786034	8.549967	-23.805873
8 (31 days)	5.664073	-23.844311	8.411353	-23.901848
9 (38 days)	5.120346	-23.877403	9.007777	-23.911241

Table 4 S/N response table for water absorption of pure epoxy

Levels		Parameter		
		A	**B**	**C**
1	Mean Free swell (%)	2.81	3.91	4.31
	Mean S/N ratio	-22.78805845*	-23.34063098*	-23.392193*
2	Mean Free swell (%)	4.5	4.18	3.78
	Mean S/N ratio	-23.57048132	-23.40968983	-23.3982912
3	Mean Free swell (%)	5.34	4.56	4.56
	Mean S/N ratio	-23.83591591	-23.44413487	-23.4039715

*means optimal parameter level

Table 5 S/N response table for water absorption of 5 % OPPs epoxy composite

Levels		Parameter		
		A	**B**	**C**
1	Mean Free swell (%)	6.03	7.00	7.22
	Mean S/N ratio	-23.43123318*	-23.59737522*	-23.6634671*
2	Mean Free swell (%)	8.55	7.62	7.54
	Mean S/N ratio	-23.70747114	-23.70599877	-23.6733046
3	Mean Free swell (%)	8.66	8.60	8.47
	Mean S/N ratio	-23.87298724	-23.70831757	-23.6749198

*means optimal parameter level

Anthony and Anthony [32] described the S/N ratio as the degree of variation when uncontrolled noise factors are present within the system. The S/N ratio used in an experiment is based on the desired quality characteristic of the process. The Taguchi method uses three main quality characteristics to describe the SN ratio: the lower-the-better (LB), the higher-the-better (HB) and the nominal-the-best (NB). In this investigation, the focus is on having the samples with the minimum water uptake of free swell. Therefore, the LB quality characteristic was chosen. The LB quality characteristic is described by Equation (2) as follows:

$$S/N = -10 Log\left(\frac{1}{n}\sum_{j=1}^{n} y_j^2\right) \quad (2)$$

where$n$ is the quantity of values obtained in each experimental trial, and y_i is each observed value.

The Taguchi optimisation provides the knowledge necessary for picking the optimal setting of parameters. Additionally, it also helps to estimate the comparative contribution and significance of each of the parameters for subsequent studies. Analysis of variance (ANOVA) was used to evaluate the contributing effect of each parameter on the quality characteristic and their individual inputs over the performance of the process. This was done by separating the total variation from the S/N response into individual contributions by parameters and errors. The total sum of squared deviations from the total mean S/N ratio, the sum of squares due to the mean for each parameter and the percentage contribution of a^{th} parameter were originally defined mathematically by Zareh et al. [33] and re-expressed for use in Equations (3) to (5) as follows:

$$SS_T = \sum_{j=1}^{n} (S/N)_i^2 - \frac{1}{n}\left[\sum_{j=1}^{n} (S/N)_j\right]^2 \quad (3)$$

where$n$ is the number of experiments in the orthogonal array, $(S/N)_j$ is the (S/N) ratio of the j^{th} experiment. The sum of squares due to the mean for each parameter is defined as:

$$SS_A = \sum_{i=1}^{m} \frac{\left(\left(\frac{S}{N}\right)_i\right)^2}{p} - \frac{1}{n}\left[\sum_{j=1}^{n}\left(\frac{S}{N}\right)_j\right]^2 \quad (4)$$

In Equation (3), m is the number of parameter levels (m = 3), j is the level number of this parameter a, $(S/N)_i$is the addition of the (S/N)ratios associated with parameter a and level j, while p is the repetition of each level of parameter a. The percentage contribution of a^{th} parameter is defined as:

$$P_A(\%) = \frac{SS_A}{SS_T} \times 100 \quad (5)$$

3. Results and discussion

While Tables 3 to 5 specify the pertinent results, the specific Tables 6 (a) and (b) summarise the data collected before and after exposing pure epoxy and OPP epoxy composites to water.

Table 6a Water absorption data for 5 % OPPs composite

S/N	Initial mass (g)			Total initial mass (g)	Final mass (g)			Total final mass (g)
	Specimen 1	Specimen 2	Specimen 3		Specimen 1	Specimen 2	Specimen 3	
1	16.88	18.12	18.86	53.86	17.65	19.07	19.53	56.25
2	16.88	18.12	18.86	53.86	17.7	19.45	19.74	56.89
3	16.88	18.12	18.86	53.86	18.11	19.8	20.27	58.18
4	16.88	18.12	18.86	53.86	18.09	19.73	20.36	58.18
5	16.88	18.12	18.86	53.86	18.34	19.86	20.42	58.62
6	16.88	18.12	18.86	53.86	18.4	19.65	20.55	58.6
7	16.88	18.12	18.86	53.86	18.31	19.83	20.32	58.46
8	16.88	18.12	18.86	53.86	18.4	19.61	20.37	58.38
9	16.88	18.12	18.86	53.86	18.42	19.98	20.3	58.7

Table 6b Summarised water absorption data for both the pure epoxy and 5 % OPPs composite

S/N	Pure epoxy			5 % OPPs composite		
	Total initial mass (g)	Total final mass (g)	Average weight gain (g)	Total initial mass (g)	Total final mass (g)	Average weight gain (g)
1	53.19	54.51	1.32	53.86	56.25	2.39
2	53.19	54.37	1.18	53.86	56.89	3.03
3	53.19	55.19	2.00	53.86	58.18	4.32
4	53.19	55.31	2.12	53.86	58.18	4.32
5	53.19	55.64	2.45	53.86	58.62	4.76
6	53.19	55.67	2.48	53.86	58.6	4.74
7	53.19	55.9	2.71	53.86	58.46	4.6
8	53.19	56.08	2.89	53.86	58.38	4.52
9	53.19	55.84	2.65	53.86	58.7	4.84

Free swell experiments were done using the Holtz and Gibbs' model. Three different samples of pure epoxy and 5 % OPP reinforced epoxy composites were prepared for this investigation. The free swell process parameters namely, initial mass, final mass and weight gain, were considered in this investigation. The initial mass is the mass of the pure epoxy/composite before dissolution, while the final mass is the mass of the epoxy/composite after 24 hours of swelling in water. The weight gain by the epoxy/composite is the difference between the final and initial masses. These parameters were taken into consideration to identify which of the samples gave the optimal swelling behaviour.

In Table 3, we obtained S/N ratios from a Taguchi experiment for the pure epoxy and 5 % OPPs reinforced composite. The S/N responses for each of the parametric levels used in this study were obtained mathematically using the arithmetic mean. In Table 3, experimental trials ranged from 3 to 38 days, representing Trials 1 to 9, respectively. It was observed that there was a direct relationship between weight gain and the length of time. This result is the same as that obtained by Kim and Seo [8]. This is also similar to the results presented by Dhakal et al. [11].

The S/N responses for each parametric level were obtained by grouping individual S/N ratios, by the level of each factor and determining their average. For instance, the S/N ratios associated with factor level A_1 for the pure epoxy are from experimental trials 1, 2 and 3 in Table 3. The associated S/N ratios were grouped together to find the mean S/N response for factor level A_1.

A_1= -22.78805
A_2 = -23.57048; and
A_3 = -23.835915

This calculation was done for all factor levels to obtain S/N responses for the pure epoxy and 5 % OPPs reinforced composites in Tables 4 and 5, respectively.

Zareh et al. [29] observed that irrespective of the quality characteristics used in the Taguchi optimisation, a higher S/N ratio signifies better quality characteristics.

The variability of the mean S/N ratios obtained for each of the parametric levels of the Taguchi experiment isdescribed graphically in Figure 2.

Thus, the factor level with the highest mean S/N response was identified as the optimal level for each of the parameters. From the results, the oil in the orange peel showed some effects on water absorption as higher resistance was developed compared to the use of epoxy resin alone, which served as a control. However, we were unable to quantify this.

FTIR analysis

The induced chemical changes and the nature of the bonds in the epoxy resin used for the experiment were studied using Fourier Transform Infrared Spectroscopy (FTIR) spectra, which were recorded using a (Bruker) FTIR spectrometer with a wave-number of the range 4000-400 cm^{-1}. This equipment was supplied from BrukerOptik GmbH, Etthingen, Germany to the Department of Chemistry, University of Lagos, Nigeria, where the experiments were conducted. FTIR was used on the samples to characterise the chemical structure for two reasons: (i) it is required to know what compounds are present in the epoxy resin to authenticate its purity and (ii) it is useful information since the chemical composition of orange peel particulate composite has not been reported.

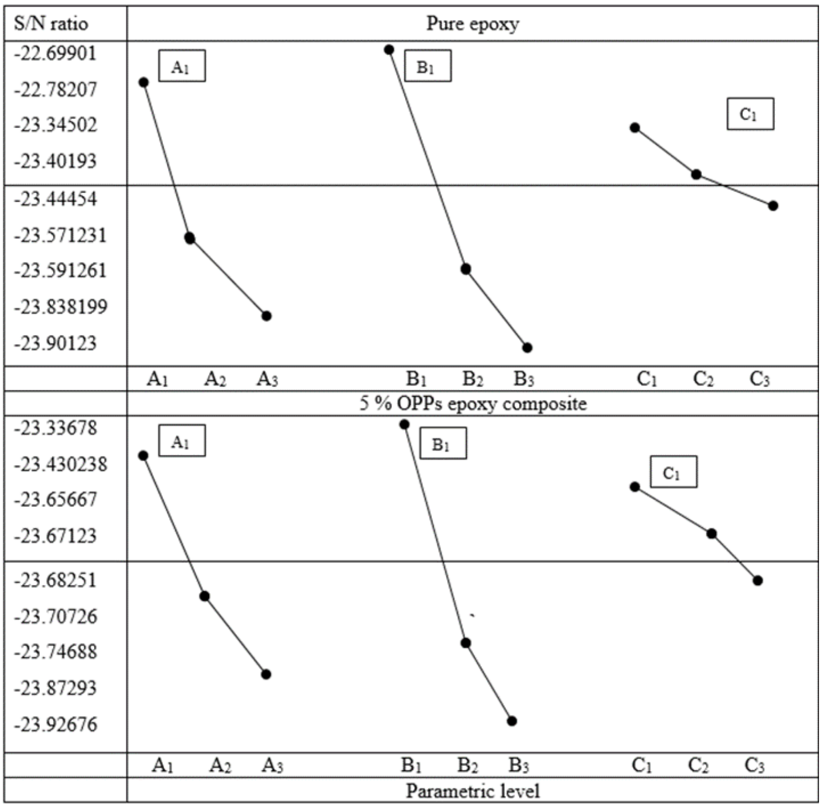


Figure 2 Main effect plots for pure epoxy and 5 % OPPs composite water absorption

Table 7a FTIR spectra relating of epoxy resins

Bond	Frequency (cm^{-1})	Intensity	Functional group
C-H stretch	3055.71	Strong	Aromatics
=C-H stretch	3055.71	Medium	Alkenes
C-H stretch	2966.05, 2926.85, 2871.76	Medium	Alkenes
N-H bend	1606.48, 1581.08	Medium	primary amines
N-O asymmetric stretch	1506.87	Strong	nitro compounds
C-C stretch (in-ring)	1455.01	Medium	Aromatics
C-H bend	1455.01	Medium	Alkanes
C-H rock	1361.92	Medium	Alkanes
N-O symmetric stretch	1295.63	Medium	nitro compounds
C-N stretch	1228.70, 1181.88, 1131.71, 1107.08, 1084.41, 1031.60	Medium	aliphatic amines
=C-N bend	970.14	Strong	Alkenes
O-H bend	913.73	Medium	Carboxylic acids
C-Cl stretch	826.45, 769.96	Medium	alkyl halides
C (triple bond) C-H: C-H bend	638.98	broad, strong	Alkynes
C-Br stretch	571.83	Medium	alkyl halides

This information will detail the composition of OPP-epoxy composites and possible reactions such groups may undergo. So, the samples characterised in these experiments are basically the epoxy resin as well as 5% OPP epoxy composites. The results of the FTIR characterization are shown in Tables 7 (a) and (b) while Figures 3(a) and (b) reflect scanning outputs. The various peaks, as revealed in the wave-number range of 4000-500 cm^{-1},were associated with various stretching and bending vibrations, as shown in Tables 7(a) and 7(b), respectively. The table of characteristic IR absorptions, prepared by the Organic Chemistry Group, Department of Chemistry and Biochemistry, University of Colorado at Boulder, USA was used in the interpretation of the FITR results (see http://orgchem.colorado.edu/ Spectroscopy/specttutor/irchart.html).

FTIR absorption tests were done on 5% OPP-epoxy composite (Table 7(b)).The results show a strong presence of alcohols and phenols (3378.59 cm^{-1}), nitro compounds (1507.64 cm^{-1}), alcohols, carboxylic acids, esters, ethers (1234.00 cm^{-1}), alcohols, carboxylic acids, esters, ethers (1181.04 cm^{-1}), alkenes (735.09 cm^{-1}), primarily,secondary amines (735.09 cm^{-1}), aromatics (735.09 cm^{-1}), primary, secondary amines (697.98 cm^{-1}) and aromatics (697.98 cm^{-1}). From this observation, the type of test that may be carried out to improve the water resistance behavior of the 5% OPP-epoxy composite was suggested.

SEM analysis

The morphological characteristics of the 5% OPP epoxy composite were studied while the interfacial bonding occurring between the particulates and the epoxy matrix was examined with the aid of scanning electron microscopy (SEM), model ASPEX 3020. The view of the samples was

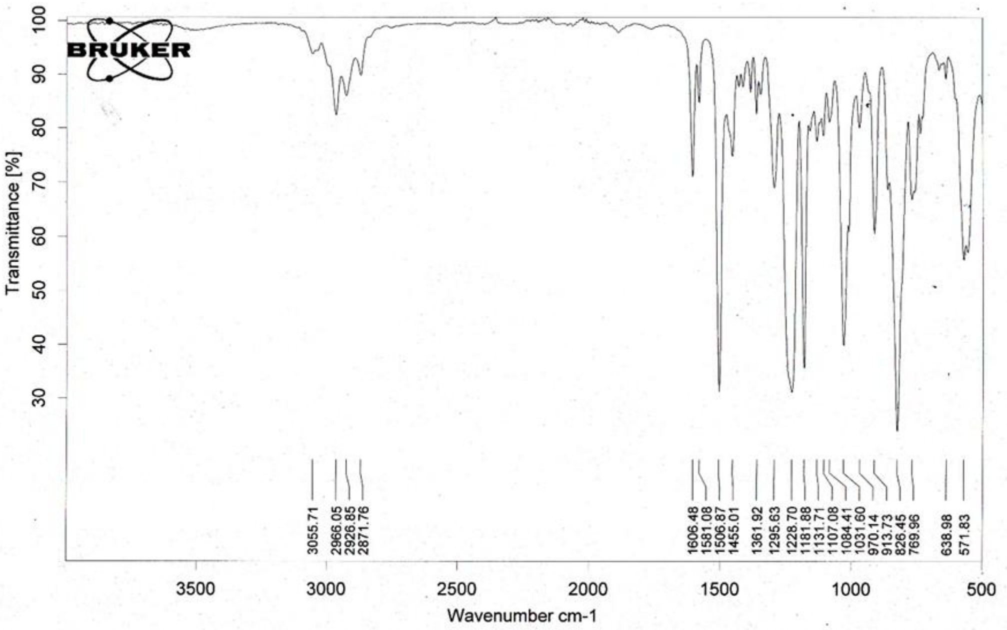


Figure 3(a) FTIR result for epoxy resin

Table 7b Results of FTIR spectra analysis for 5% OPP epoxy composite

Bond	Frequency (cm^{-1})	Intensity	Functional group
O-H stretch, H-bonded	3378.59	strong, broad	alcohols, phenols
O-H stretch	2924.52, 2869.16	Medium	Carboxylic acids
N-H bend	1606.10, 1580.96	Medium	primary amines
N-O asymmetric stretch	1507.64	Strong	nitro compounds
C-C stretch (in-ring)	1454.97	Medium	Aromatics
C-H bend	1454.97	Medium	Alkanes
-	1382.69, 1361.80	-	-
C-H wag (-CH_2X)	1294.42	Medium	alkyl halides
C-H wag (-CH2X)	1294.42	Medium	alkyl halides
C-O stretch	1234.00	Strong	alcohols, carboxylic acids, esters, ethers
C-H wag (-CH_2X)	1234.00	Medium	alkyl halides
C-H wag (-CH2X)	1234.00	Medium	alkyl halides
C-O stretch	1181.04	Strong	alcohols, carboxylic acids, esters, ethers
C-H wag (-CH_2X)	1181.04	Medium	alkyl halides
C-H wag (-CH2X)	1181.04	Medium	alkyl halides
C-N stretch	1105.22, 1082.77, 1030.97	Medium	aliphatic amines
C-Cl stretch	826.48	Medium	alkyl halides
=C-H bend	735.09	Strong	Alkenes
N-H wag	735.09	strong, broad	primary, secondary amines
C-H “opp”	735.09	Strong	Aromatics
C-Cl stretch	735.09	Medium	alkyl halides
N-H wag	697.98	strong, broad	primary, secondary amines
C-H “opp”	697.98	Strong	Aromatics
C-Cl stretch	697.98	Medium	alkyl halides
C-Cl stretch	557.01	Medium	alkyl halides
C-Br stretch	557.01	Medium	alkyl halides

perpendicular to the fractured surface. Micrographs with magnifications of 200X and 2000X were made. For the SEM morphologies of 5% OPP-based epoxy composite surfaces after immersion in water (Figure 4), gaps between the particulate filler and the matrix were observed, indicating poor adhesion. The SEM morphologies of the surface of a dry 5% OPP-based epoxy composite (Figure 5) also revealed poor adhesion but not to the degree of the samples that had been immersed in water. Figure 6 shows SEM morphologies of pure epoxy (wet), which has fewer gaps. In Figure 7, the adhesion was stronger and no pronounced gaps are noticeable. Surface treatment is therefore proposed for the improvement of the adhesive properties of OPP epoxy composites. These gaps were seen in the 200X and 2000X magnifications of samples.

The results of the ANOVA ($p<0.05$) for the pure epoxy and 5 % OPPs reinforced composite are shown in Tables 8 and 9, respectively. According to the results for the pure epoxy, the final mass (55.98 %) was found to have the highest percentage contribution to water absorption, closely followed by the influence of the initial mass (43.33 %). The final mass had the strongest influence because water absorption was enhanced by the overall mass. Thus, as the epoxy attained a new mass it absorbed more water across its entire surface area. Weight gain was found to have the lowest influence on the water absorption of the epoxy and was considered insignificant as a pooled error. From the ANOVA results for the 5% OPPs composite, the influence of the final mass on the water absorption was pronounced at 64.52 % than for pure epoxy. This could be attributed to the presence

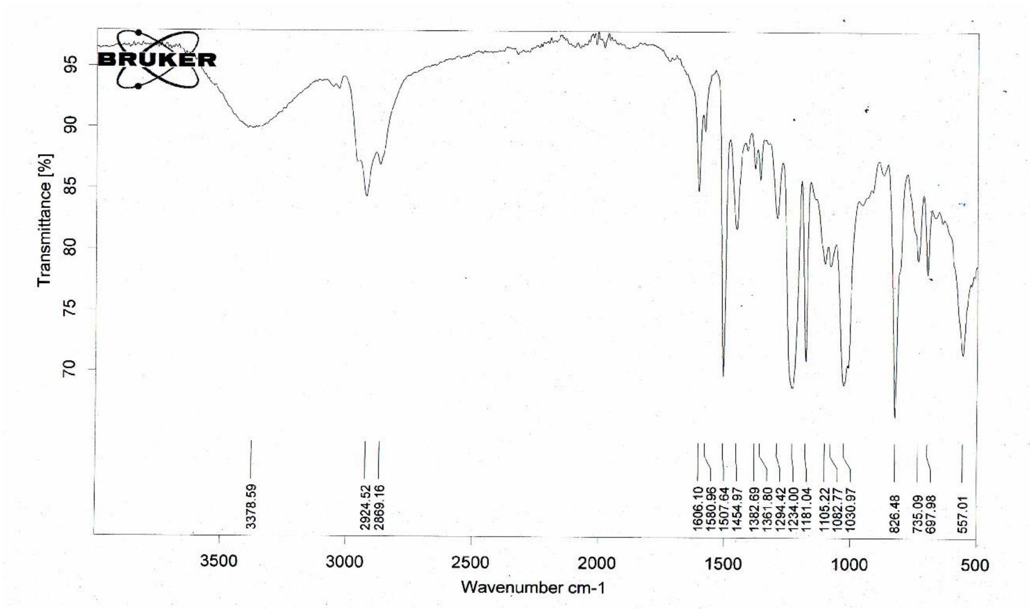
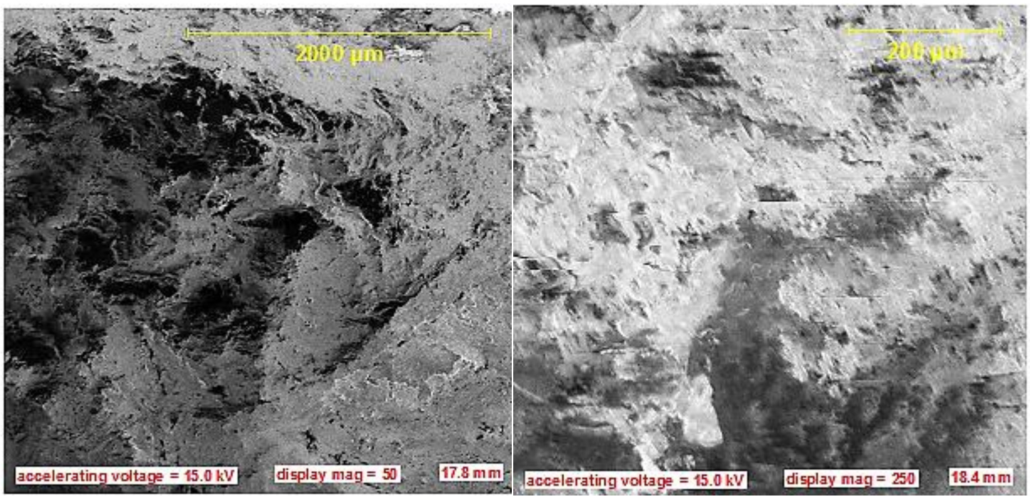
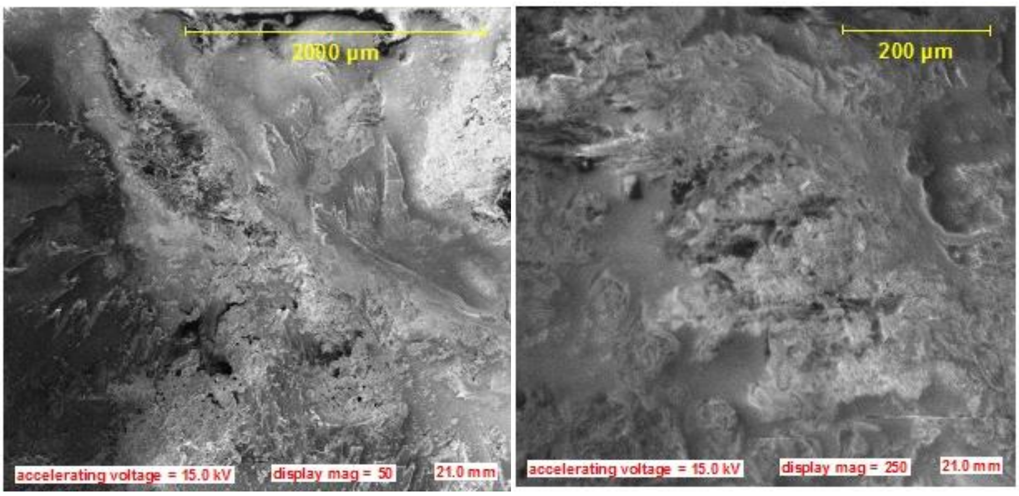


Figure 3(b) FTIR result for 5% OPP epoxy composite



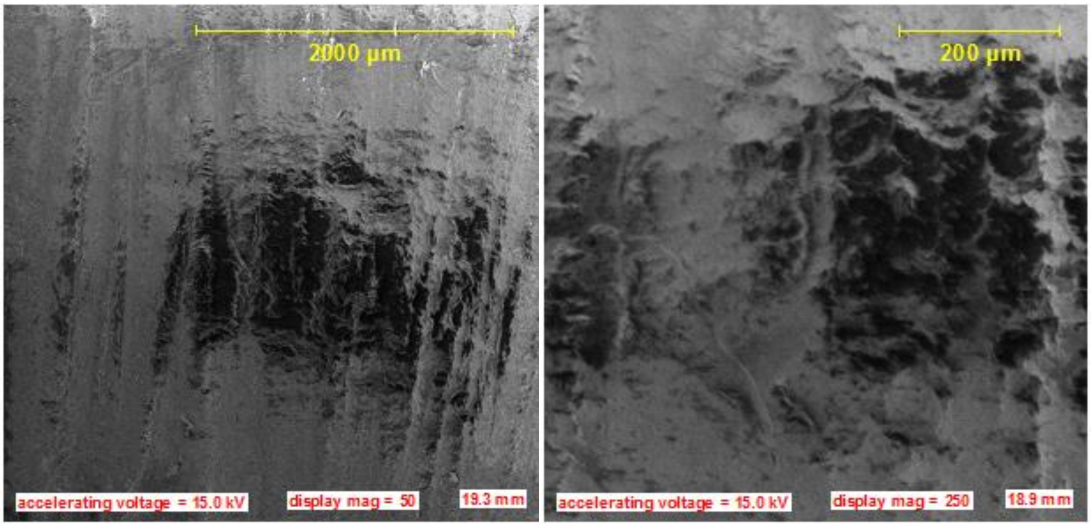
(a) (b)

Figure 4 SEM morphologies of surface 5% OPP-based epoxy composite inserted in water (a) low magnification. (b) high magnification



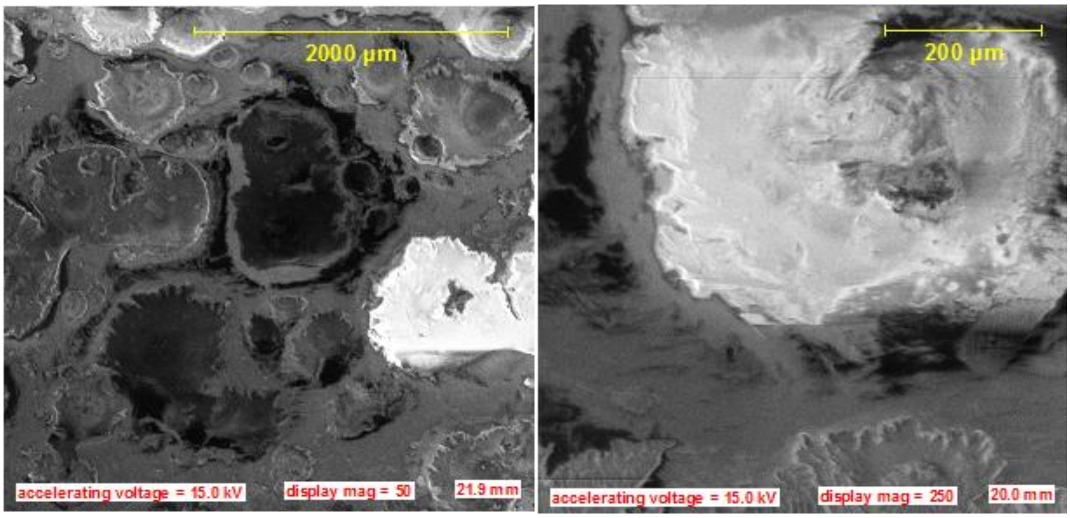
(a) (b)

Figure 5 SEM morphologies of surface of dry 5% OPP-based epoxy composite (a) low magnification (b) high magnification



(a) (b)

Figure 6 SEM morphologies of pure epoxy (wet) (a) low magnification (c) high magnification



(a) (b)

Figure 7 SEM morphologies of pure epoxy (dry) (a) low magnification (b) high magnification

Table 8 Analysis of variance table for water absorption of pure epoxy

Parameter	Degree of freedom	Sum of squares	Mean square	Contribution (%)
A	2	1.809	0.905	43.33
B	2	2.338	1.169	55.9765
**C*	2	0.0149	0.0074	0.358
Total	6	4.1759	2.0879	100
(Error)	0	0.0139	0.0069	0.3355

* pooled error

** ($p<0.05$)

of orange peel particles in the composite that increased the final mass and capacity for water absorption. The initial mass had a percentage contribution of 35.30 % to the water absorption, while the weight gain had the least contribution of 0.1184 % and was regarded as a pooled error.

An investigation was launched to find the most significant factor levels and mean S/N ratios needed for water absorption optimisation of the pure epoxy and 5 % OPPs reinforced composite. This was done by applying the Pareto 80-20 rule to the factor levels and the mean S/N ratios for both materials before performing Taguchioptimisation.

Taguchi-Pareto (factor level-based)

The Pareto 80-20 rule was applied to the table of parameters and levels for the water absorption experiment using pure epoxy and 5 % OPPs composite. This was done to identify the factor levels that significantly contribute to optimisation of water absorption. The factor levels for each of the materials were arranged in descending order. The total sum, percentage contribution and cumulative percentage contribution of each value was obtained. At the 80 % threshold, the values were used to form a revised table of parameters and levels described (Table 10), while the values

Table 9 Analysis of variance table for water absorption of 5 % OPPs epoxy composite

Parameter	Degree of freedom	Sum of squares	Mean square	Contribution (%)
A	2	0.3001	0.15	35.30
B	2	0.5486	0.2743	64.5174
**C*	2	0.0010	0.0005	0.1184
Total	6	0.85031	0.4251	100
(Error)	0	0.00053	0.00026	0.0642

* pooled error

** ($p<0.05$)

Table 10 Revised parameters and levels for the water absorption experiment

Pure Epoxy			
Levels	**Parameters**		
	Initial mass, M_i (g)	**Final mass, M_f (g)**	**Weight gain, W_g (g)**
1		15.62	
2	18.47	19.25	
3	19.6	20.52	
5 % OPPs reinforced composite			
1		17.96	
2	18.12	19.66	
3	18.86	20.41	

in the 20% region were not considered for further optimisation.

Applying the Taguchi method using the factor levels, a response (Taguchi-Pareto S/N response) was derived. The missing factor levels in the new table: A_1, C_1, C_2 and C_3, were not economical for optimality and not considered. A new optimal parametric setting was obtained as A_2B_1. The same trend of results was obtained using the Taguchi method for the revised table of parameters and levels for the 5 % OPPs reinforced composite. The missing factor levels A_1, C_1, C_2 and C_3, were not economical for optimality.

Taguchi-Pareto (S/N response-based)

The Pareto 80-20 rule was applied to the water absorption S/N response tables of pure epoxy and 5 % OPPs composite. This was done to determine which of the mean S/N ratios were significant to the optimisation of the water absorption parameters of the materials. The S/N ratios were arranged in descending order. The sum of the S/N ratios was calculated and their percentage contributions to the total sum were determined. The cumulative percentage contribution was calculated. A cumulative percentage of 80 % was used as the threshold. The S/N ratios below the threshold were cut-off because they were not economical for optimisation, while the remaining S/N ratios were used to develop revised S/N response tables. In the revised table (Table 11) for the pure epoxy, S/N ratios for factor level positions A_2 and A_3 are missing, indicating that they were not economical for optimality.S/N ratios were missing for A_3 and B_3. The revised S/N response table for water absorption of 5 % OPPs epoxy composite is shown in Table 12.

There are a number of target applications of these OPP epoxy composites. In agriculture, heavy components made of metals can be replaced with the OPP-epoxy composite materials. In engines of blowers in removing chaff from crops during harvest, the parts could be replaced with lightweight OPP epoxy composites. Another target application is in agricultural crop storage. Crops may be stored in small containers that permit free movement of air. In such a situation, an OPP epoxy composite could be used as a coating applied to inhibit corrosion. They may also be applied to the wear surfaces of tools.

4. Conclusions

In this work, the following principal issues were learnt: (1) The principles of the Holtz and Gibbs' model for expansive particulates assisted in composite development, by providing information relevant to whether or not the composite's free swell reached the threshold limit for safety; (2) Taguchi could be an instrument to establish the best possible setting of water absorption parameters for the minimal swelling of he composite; (3) Taguchi-Pareto is an instrument to determine the factors that are economical from the perspective of optimality, using the 80-20 priority rule; (4) ANOVA is a tool to ascertain the individual contributions of each parameter in the water absorption process.

From a detailed consideration, the summaries are given:

Water absorption properties of pure epoxy and 5 % OPPs composite

For all the nine periodic measurements taken, the water absorption of the 5 % OPP reinforced epoxy were found to be greater than that of pure epoxy, owing to the presence of orange peel particles within the composite. Orange peel particulate composites absorb more water than pure epoxy.

- The highest percentage of water absorption for the pure epoxy and composite was obtained in the eighth and ninth measurements, respectively. This showed that water absorption progressed with continued immersion in water.

Taguchi optimization

- Using the LB quality characteristics, the optimal parametric setting for the pure epoxy and 5 % OPPs reinforced composite was found at $A_1B_1C_1$ for both materials. This shows that the least valued parameter will produce the minimal water absorption of free swell.
- For the pure epoxy, the optimal setting for the parameters corresponded to the lower free swell values except for parameter *C*, where the lower water absorption was recorded at level 2.
- Alternatively, the optimal setting for the 5 % OPPs composite corresponded to lower water absorption values across all the parameters.
- Overall, the application of the Taguchi method was successful in optimising the water absorption properties of the materials.

Analysis of variance (ANOVA)

- The application of ANOVA helped to identify the significance of each parameter through their percentage contributions.

Table 11 Revised S/N response table for water absorption of pure epoxy

Levels		Parameter		
		A	***B***	***C***
1	Mean Free swell (%)	2.81	3.91	4.31
	Mean S/N ratio	-22.782075*	-23.34063*	-23.39219*
2	Mean Free swell (%)	4.5	4.18	3.78
	Mean S/N ratio		-23.40969	-23.39829
3	Mean Free swell (%)	5.34	4.56	4.56
	Mean S/N ratio		-23.444135	-23.40397

*means optimal parameter level

Table 12 Revised S/N response table for water absorption of 5 % OPPs epoxy composite

Levels		Parameter		
		A	***B***	***C***
1	Mean Free swell (%)	6.03	7.00	7.22
	Mean S/N ratio	-23.43123*	-23.597375*	-23.66347*
2	Mean Free swell (%)	8.55	7.62	7.54
	Mean S/N ratio	-23.70747	-23.705999	-23.67330
3	Mean Free swell (%)	8.66	8.60	8.47
	Mean S/N ratio			-23.67492

*means optimal parameter level

- The final mass is the most significant parameter for both materials, with a higher percentage contribution, while the weight gain gave the least percentage contribution and was considered an error term.

Taguchi-Pareto analysis

- The use of the Pareto 80-20 rule in combination with Taguchi optimisation of the factor levels underscored the results of the ANOVA, which identified the final mass and weight gain to have high and low significance, respectively.

5. Acknowledgement

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