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A Method of Large-Scale Resource Utilization of Algae—Eutrophic Waste from Lake Chao, China: Preparation and Performance Optimization of Composite Packaging Materials

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Abstract: In order to realize the resource utilization of bloom algae from Lake Chao, this study presents the use of fresh algae to improve the mechanical and biological properties of low-density polyethylene (LDPE). In this study, the algae and LDPE were used as raw materials, maleic anhydride grafted polyethylene (PE-g-MAH), polyethylene wax (PE-wax) and white oil, and glycerin were used as the compatibilizer, lubricant, and plasticizer, respectively. The single factor experiments were conducted with these three individual factors, and the response surface methodology technique was used to optimize the process conditions. In the single factor experiments, the mechanical properties of the composites increased with additions of PE-g-MAH, PE-wax/white oil, and glycerin. Both flexural strength and flexural modulus were maximized to optimize the preparation conditions. The optimum preparation conditions were found as follows: algae powder of 15.00 wt%, LDPE of 85.00 wt%, PE-g-MAH of 4.00 wt%, lubricant of 2.67 wt%, and glycerin of 3.00 wt%. This resulted in 11.60 MPa of tensile strength, 9.95 MPa of flexural strength, and 241.00 MPa of flexural modulus. The mechanical properties of composites were greatly improved compared with the absence of additives. In addition, compared with LDPE resin, the degradability of the composite was improved, and the weight loss rate was 7.73% after 6 months. The results recommended that the composites of the algae from Lake Chao and LDPE resin could be a useful material in the packaging field. Generally, the prepared composite particles can be used to produce foam products, packaging bags, or hard packing boxes with special shapes. It is more environmentally friendly, and more able to meet the challenges of sustainable development.

Keywords: fresh algae; packing material; response surface methodology; degradation performance

1. Introduction

In recent years, algal bloom phenomena have occurred frequently in Lake Chao, which is one of the five largest freshwater lakes in China. Every year between June and September, the algae in Lake Chao exhibit exponential growth. As shown in Figure 1, a schematic view of algal bloom in Lake Chao on June 12, 2013, according to a news release on the China meteorological website, showing that the algae cover a relatively large area. Chao Lake waters are known to cover an area of approximately 560 to 825 km^2 [1], the blue-green algae cover area is estimated to be about 18 km^2 and the coverage rate is about 3.00%. Lake Chao is an important source of water for Hefei in Anhui Province, so the occurrence of algal bloom significantly damages its ecological structure and poses a threat to biological safety [2]. The algae on the surface of Lake Chao have become a large solid waste that is difficult to dispose. If the algal waste on the surface of the water body cannot be cleaned up in time, it will grow and multiply throughout the entire lake. Thus, it will encroach on the living space of the aquatic organisms and threaten their life and health.

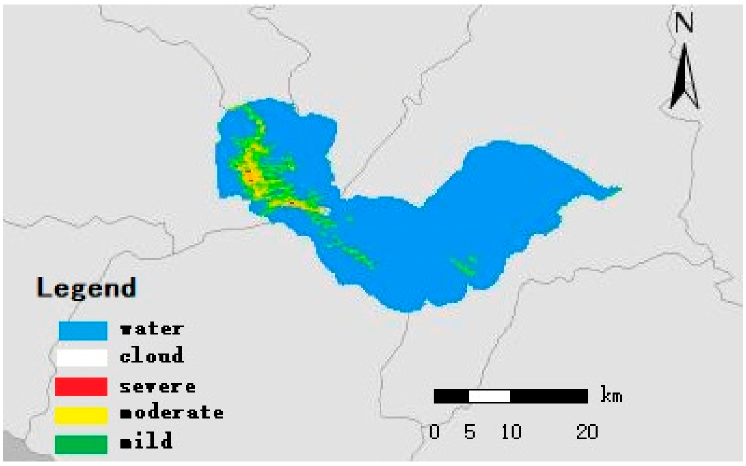


Figure 1. Schematic diagram of water bloom intensity in Lake Chao.

The dominant species in the algal bloom is microcystis aeruginosa, which forms small molecular peptides and toxic substances in the algal cells [3,4]. This kind of algal toxin can cause protein over-phosphorylation in animals and induce significant changes in their cellular morphology, structure, and function, which can lead to liver tumors. Therefore, it is urgent to find a suitable method to handle these algal blooms in Lake Chao. Although there are many works on utilizing blue-green algae in Lake Chao, they are mainly focused on biogas production and low-end fertilizers, which have low added value, low economic benefit, and low scalability [5]. There are also studies on the extraction of algal proteins and exopolysaccharides from the Lake Chao algae [6–9]. Although the added value of these products is improved, the extraction process is complicated and the production cost is high, which is not an effective approach to consume large amounts of algae.

As one of the main raw materials of film packaging materials, low-density polyethylene resin is known to be used in a large amount and has a long degradation period. At the same time, in the field of biodegradable materials, there are many cases of introducing biological components into resin matrix to give us some inspiration. From previous studies that produced bioplastics from starch, protein or inorganic filer [10–14], considering that algae from Lake Chao are rich in phyco-protein and polysaccharide [15–19], if the properties of the biomacromolecules can be changed through physical or chemical means, the biomacromolecules can be used to prepare plastic products [20–25]. For example, edible biofilms or packaging materials were prepared using starch and protein as raw materials or by using the properties of hydroxyl groups in protein macromolecules grafted with compatibilizers [26,27], such as maleic anhydride, by introducing biomacromolecules into the low-density polyethylene (LDPE) chain [28,29]. Through experimentation, we can not only analyze the feasibility of the experimental methods based on the test results of the mechanical properties of the composites, but we can also analyze the behavior of the Lake Chao algae powder and LDPE during preparation using the optical properties of the material. For example, the benzene rings containing tyrosine, L-phenylalanine, and tryptophan residues, and the protein molecules contain conjugated double bonds that give the protein its ultraviolet absorption properties. The characteristic functional group of the reaction materials also appears as the corresponding characteristic absorption peak in the infrared spectrum [30].

In recent years, the production of bioplastics from microalgae is a hot topic. At present, this kind of research mainly uses the extract of biomass such as lipid from microalgae as culture medium [31–34] or a single algae species as bioreactor [35–39] to produce bioplastics. The production cost is high and the yield is low. In this paper, the raw material of polyethylene bioplastics was directly prepared from wild algae. The algae from Lake Chao could be obtained as algae powder through simple mechanical and physical drying. The mode of production is of great significance for the resource utilization of algae from algal bloom, and its production cost is lower and it is more adaptable to market demand. The combination of the Lake Chao algae powder with the LDPE material can provide a more extensive and direct treatment for algae harvested through mechanical fishing. A new concept to solve the algal bloom algae for this rich-in-protein waste is to provide a reasonable way to use it [40]. Moreover, the indirect removal of nitrogen, phosphorus, and other elements in Chao Lake in this way is a very important step to reduce lake eutrophication. Thus, the flexural properties of the LDPE can be improved by the addition of Lake Chao algae powder. As LDPE reins are mainly used in packaging field, the flexural properties of the composite materials are further optimized so that they satisfy a broader market demand. In addition, the production cost of algae powder of Lake Chao is low, and the application of algae powder from Lake Chao is equivalent to indirectly reducing the production cost of LDPE materials. Finally, the use of algal bloom algae powder as a raw material to prepare composites combined with LDPE is equivalent to replacing the use of part of the LDPE resin, which indirectly reduces the use of plastic products to improve their degradation properties. Moreover, research on the preparation of bio-plastics from algae powder is rare, so this work is expected to provide some concepts and references to develop and research new biodegradable materials in the future.

2. Materials and Methods

2.1. Materials

Fresh algae were collected from the western half of Lake Chao, 15 cm away from the surface waters. The algae were directly salvaged from the lake, filtered with gauze to remove some of the water content, and then brought back to the laboratory for cryopreservation (−10 °C). The soil was collected from farmland along the coast of Chao Lake and screened and placed in a 40 cm diameter flower pot. The LDPE was purchased from Dongguan Jiuma Plastic Industry Co., Ltd (China), maleic anhydride grafted polyethylene (PE-g-MAH) was purchased from Hefei Youshuo Scientific Instrument Co., Ltd (China), polyethylene wax (PE-wax) was purchased from Anhui Jiuyi Chemical Co., Ltd. (China), white oil was purchased from Guangzhou Teyun Trading Co., Ltd. (China), and glycerin was purchased from Wuxi Yatai United Chemical Co., Ltd. (China). All materials were used directly without further purification.

2.2. Preparation of Algae Powder

The frozen algae were taken from the frozen warehouse, thawed at room temperature, and laid in a tray. The thickness was less than 2 mm, and the sample was dried in a microwave vacuum drying oven. The drying conditions were 40 °C, 700 w/h, and a vacuum degree of 0.08. After drying for 60 minutes, the dried flaky algae were crushed by a pulverizer and the particles, with a particle size less than 0.15 mm, were collected and sealed for preservation.

2.3. Design Experiments

2.3.1. Single Factor Experiments

Assume that the total mass of algae powder and LDPE was 100.00 wt%, the addition of other materials was relative to this total mass.

In order to study whether the algae powder can be blended with LDPE suitably, six groups of parallel experiments were designed to prepare the algae powder/LDPE composites. The blue algae powder was added at 0.00, 5.00, 10.00, 15.00, 20.00, and 25.00 wt%, the addition of any other additives was 0. These materials were mixed with LDPE in turn with high speed mixer at 110–115 °C for 5 min. The twin-screw setting temperature was 125–145 °C for the extrusion granulation, and the temperature of the injection molding machine was 160 °C. The sample was kept in the dryer for 24 hours for later testing. The experiments were repeated 3 times in each group, and the results were averaged.

To study the effects of the compatibilizer (PE-g-MAH) content on the performance of the composites, six sets of experiments were designed to prepare the algae powder/LDPE composites. The addition of algae powder was 15.00 wt%, the addition of PE-g-MAH was 0.00, 1.00, 2.00, 3.00, 4.00, 5.00 wt%, the addition of other additives was 0. The samples were prepared with LDPE in the same manner as description in the previous paragraph. The experiments were repeated 3 times in each group, and the results were averaged.

To study the effects of the lubricant (PE-wax and white oil) content on the performance of the composites, six sets of experiments were designed to prepare the algae powder/LDPE composites. The addition of algae powder was 15.00 wt%, the additions of PE-wax and white oil were 0.00, 1.00 and 0.33 wt%, 2.00 and 0.67 wt%, 3.00 and 1.00 wt%, 4.00 and 1.33 wt%, 5.00 and 1.67 wt%, respectively. The addition of other additives was 0. The samples were prepared with LDPE in the same manner as description in the second paragraph. The experiments were repeated 3 times in each group, and the results were averaged.

To study the effects of the plasticizer (glycerin) content on the performance of the composites, six sets of experiments were designed to prepare the algae powder/LDPE composites. The addition of algae powder was 15.00 wt%, the addition of glycerin was 0.00, 1.00, 2.00, 3.00, 4.00, 5.00 wt%. The addition of other additives was 0. The samples were prepared with LDPE in the same manner as description in the second paragraph. The experiments were repeated 3 times in each group, and the results were averaged.

2.3.2. Design Experiment Based on Response Surface Method

Based on the single factor experiments, three factors have an effect on the properties of the composites. In order to further optimize the properties of the composites, the Box–Benhnken response surface method was used to design the experimental scheme, and the interaction between the factors was analyzed. The content of compatibilizer, lubricant, and plasticizer were the independent variables, and the flexural properties of the composite were the response values.

The Design Expert 8.0.6 software was used to analyze the experimental data, and a regression analysis was performed on the interactions between the factors. Experiments were conducted to verify the optimal experimental scheme predicted by the model. Each group was repeated 3 times.

2.4. Weight Loss Rate Experiment

The LDPE resin particles and the prepared composite particles were blown into a thin film with a thickness of about 0.08 mm. The films were cut into 4 × 4 cm squares, washed, dried, and weighed for 24 h (105 °C), then buried in several flowerpots about 15 cm from the surface of the soil, and watered regularly to keep the soil moist. The buried square thin films were dug out at intervals of 15 days, washed, dried, and weighed for 24 hours (105 °C), and the weight loss rate was calculated.

2.5. Measurements and Characterization

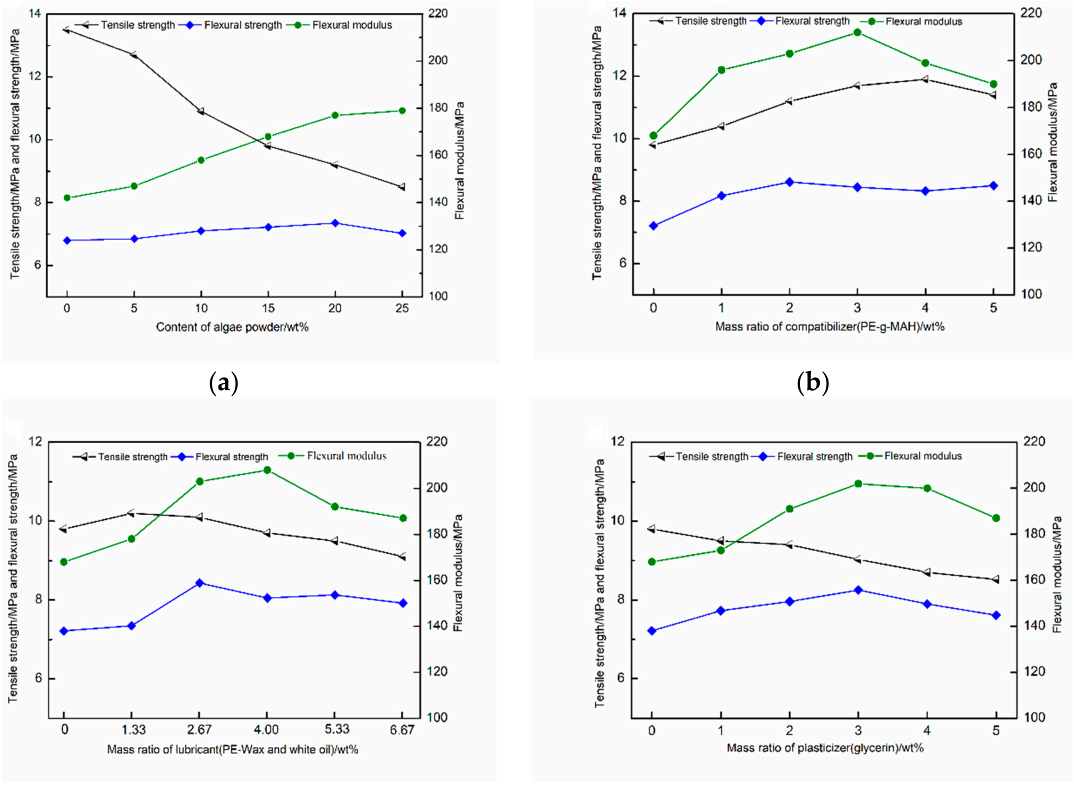
The tensile properties of the prepared algae powder/LDPE composites were tested in accordance with ISO527-2:1993 at a speed of 5 mm/min. The flexural properties were examined according to ISO178:1993 at a speed of 2 mm/min.

The algae powder of these two groups, which had been plasticized by glycerin, were scanned by infrared spectrum, the weight of glycerin to algae powder was 20.00% and 33.33%, corresponding to the experiment of adding 3.00 and 5.00 wt% of glycerin in the last paragraph of Section 2.3. In addition, the algae powder, LDPE, PE-g-MAH, and the composites were all subjected to Fourier transform infrared (FTIR) spectroscopy with a scanning wave band of 500~4000 cm^{-1}.

3. Results and Discussions

3.1. Analysis of Single Factor Experimental Results

The single factor experimental results are shown in Figure 2; the content of the algae powder in Figure 2a is taken as the single variable, when the content of algae powder increases from 0 to 25.00 wt%, the tensile strength dropped by 37.04% from 13.50 to 8.50 MPa. On the contrary, the flexural strength and modulus show an increasing trend. The flexural strength and modulus increase from 6.80 and 142.00 MPa to 7.02 and 179.00 MPa, respectively. The possible reasons for this variation phenomenon are as follows, when the content of algae powder is low, it can be dispersed in the system. With the increase of algae powder, the tensile properties of the composites decrease significantly, due to the agglomerate of particles at the force of hydrogen bonds. In the meantime, the increased rigidity of the composites is attributed to the addition of algae powder.



(**a**) (**b**)

(**c**) (**d**)

Figure 2. Effect of algae powder content (**a**), compatibilizer (PE-g-MAH) addition (**b**), lubricant (PE-wax and white oil) addition (**c**), and plasticizer (glycerin) addition (**d**) on mechanical properties of the composites.

As shown in Figure 2b, in the compatibilizer (PE-g-MAH) single factor experiments, the addition of PE-g-MAH increased from 0 to 5.00 wt%. As a result, the tensile strength, flexural strength, and flexural modulus of algae powder/LDPE composites are all increased, the flexural strength and modulus decrease when the content is more than 3.00 wt%. From the initial 9.80, 7.22, and 168.00 MPa, with the increase of the addition of PE-g-MAH, the maximum tensile strength is 11.90 MPa when the content of PE-g-MAH is 4.00 wt%. The maximum value of flexural strength is 8.62 MPa when the addition is 2.00 wt%, and the maximum value of flexural modulus is 212.00 MPa when the addition was 3.00 wt%. The shearing action of the twin-screw extruder provided a condition for the contact reaction between PE-g-MAH and algae powder. In the early stage, the mechanical properties of algae powder/LDPE composites are improved. This is possibly due to the addition of PE-g-MAH, and the special molecular structure of PE-g-MAH. It can be esterified with a functional group of algae powder by an anhydride group at one end and tightly entwined with the substrate by polarity similar to LDPE resin at the other end, which formed a link between the macromolecules in the algae powder and the LDPE molecules via graft copolymerization. This led to enhanced tensile and flexural properties of the composites. When the amount of PE-g-MAH is excessive, this part will not participate in the reaction and will have a negative impact to the mechanical properties of the composites.

Figure 2c shows the effect of lubricant (PE-wax and white oil) addition on the mechanical properties of algae powder/LDPE composites. In Figure 2c, the tensile strength of the composites remained relatively stable at approximately 10.00 MPa, with an increase in the lubricant addition. The flexural strength and flexural modulus show a trend of increasing initially, decreasing slowly, and then tending to be stable. The possible reason is that the use of the lubricant reduced the friction between the material molecules as well as the friction of the mold. Therefore, the smoothness of the spline is improved, and the flexural performance is enhanced. When the addition of the lubricant is 2.67 wt %, the flexural strength and flexural modulus of the material shows high values of 8.43 and 203.00 MPa, respectively. However, with the increase of the lubricant addition, the poor compatibility between the white oil and the resin material caused problems of press-out, which led to the appearance of white oil on the surface of the material and affected its flexural properties.

As can be seen in Figure 2d, the effect of plasticizer (glycerin) on the mechanical properties of the algae powder/LDPE composites is investigated. The addition of algae powder is 15.00 wt%. In this single factor experiments, the tensile strength of the composites decreases slowly from 9.80 to 8.52 MPa, a decrease of 13.06% in the process of increasing the addition of glycerin from 0 to 5.00 wt%. On the contrary, the flexural strength and flexural modulus of the composites show increasing at first and a slight decrease or a tendency to stabilize, and reach the maximum values when the glycerol addition is 3.00 wt%, which are 8.25 and 202.00 MPa, respectively. The reason for this trend is probably due to the fact that the addition of glycerin weakens the hydrogen bonds between or within the molecules of algae powder, the molecular chain mobility is increased and the crystallinity is decreased. When the glycerin is excessively added, the flexibility of the molecular segment of algae powder is increased, and the ability to resist bending is decreased, which is manifested as a decrease in flexural properties.

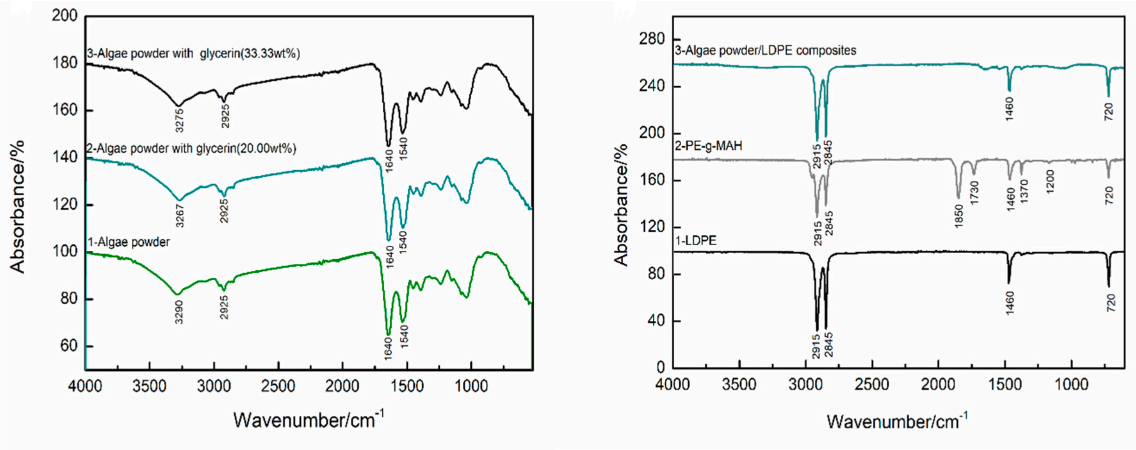
3.2. Behavioral Characterization of the Combined Algae Powder and LDPE Resin

It is known that infrared spectroscopy can be used as a method to identify hydrogen bond interactions [41]. Based on the simple harmonic oscillator model, the change of force constant Δf can be expressed as follow [42]:

$$\Delta f = f_{\mathrm{p}} - f_{\mathrm{np}} = \mu\left({v_{\mathrm{np}}}^2 - {v_{\mathrm{p}}}^2\right)/4\pi^2, \tag{1}$$

where μ represents the reduced mass of the simple harmonic oscillator, $\mu = \mathrm{m_1 m_2}/(\mathrm{m_1} + \mathrm{m_2})$. v is the vibration frequency (wavenumber), np and p represent the oscillator before and after plasticization, respectively. According to the Equation (1), the change of the force constant is directly related to the change of the stretching vibration frequency. Therefore, greater change of the frequency (wavenumber) in infrared spectrum before and after plasticization, the greater change of the force constant (Δf), the greater ability to weaken the hydrogen bond, too.

Figure 3 shows the effect of glycerin content on the hydrogen bond in algae powder and possible structural changes during the preparation of algae powder/LDPE composites. In Figure 3a, the infrared spectrum for the bottom layer of the algae powder shows a stretching vibration peak for O-H near 3290 cm^{-1}, a band near 2925 cm^{-1} should be the stretching vibration peak of N-H or the stretching vibration peak of saturated C-H, and the two characteristic bands of 1640 and 1540 cm^{-1} in the region of 1500–1950 cm^{-1}, should be the stretching vibration peak of C = O and the symmetrical bending vibration peak of N-H. The characteristic absorption peak conformed to the peak of the amide bond.



(**a**) (**b**)

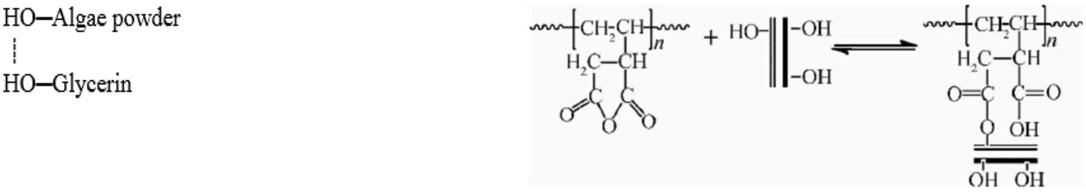
Figure 3. FTIR spectrum of algae powder and several rein materials. Infrared spectrum of algae powder before and after plasticizing (**a**) and infrared spectra of the main thermoplastic materials in the preparation of composites (**b**).

As shown in Figure 3a, the infrared spectrum for the middle and upper layers represent the infrared spectra of the algae powder with 20.00 and 33.33 wt% glycerin plasticized, respectively. The O-H wave number decreases from 3290 to 3267 and 3275 cm^{-1}.

According to Equation (1), the effect of plasticizer content on the hydrogen bond force constant is calculated [43]. The calculation results are shown in Table 1. It can be seen that with the increase of glycerin content, the change of the force constant of hydrogen bond first increases and then decreases, reflecting that the addition of glycerin can weaken the force of hydrogen bond in the algae powder, but when the glycerin content exceeds a certain proportion, the hydrogen bonds are more easily formed between the glycerin molecules. At this time, the ability to weaken the hydrogen bonds in algae powder is reduced, showing a decrease in the value of Δf. This indicates that the formation of hydrogen bonds between molecules in glycerin and algae powder, as shown in Figure 4a. The hydrogen bond acceptor is the hydrogen in the hydroxyl group of the algae powder, and the donor is the oxygen atom in the glycerol hydroxyl group, which weakens the hydrogen bond between molecules of the algae powder and the stretching vibration frequency of O-H [44].

Table 1. Δf of hydrogen bonds in algae powder with different glycerin content.

Sample	Wave Number of O-H	Δf
Algae powder	3290	-
Algae powder with glycerin (20.00 wt%)	3267	3599
Algae powder with glycerin (33.33 wt%)	3275	2350



(**a**) (**b**)

Figure 4. The possible hydrogen bonds between glycerin and algae powder (**a**) and reaction mechanism of PE-g-MAH and algae powder (**b**).

The infrared spectra of LDPE resin locate in the lower layer of Figure 3b, the stretching vibration absorption peak of saturated C-H appears at 2915 and 2845 cm^{-1}, and the bending vibration peak of saturated C-H appears at 1460 cm^{-1}. There is an out-of-plane flexural vibration characteristic band of unsaturated C-H around 720 cm^{-1}, which corresponds to the characteristic group of olefins. The PE-g-MAH characteristic absorption spectrum locates in the middle layer of Figure 3b, except for the saturated C-H peak at 2915, 2845, and 1460 cm^{-1} and the unsaturated C-H peak at 720 cm^{-1}, the antisymmetric and symmetric stretching peaks of C = O in acid anhydrides appear at 1850 and 1730 cm^{-1}. In addition, the C-O-C stretching vibration peak appears at about 1200 cm^{-1}, while the infrared spectra of the algae powder/LDPE composites in the upper layer is basically the same as that of the base material LDPE. The characteristic absorption peaks of the anhydride group in PE-g-MAH and the blend powder in Figure 3a are weakened or disappear. It is inferred where not only the physical reaction but also the esterification reaction takes place as shown in Figure 4b during the preparation of composites [30].

3.3. Optimization of the Algae Powder/LDPE Composites Mechanical Properties Using Response Surface Methodology

3.3.1. Response Surface Methodology Advantage

Response surface methodology (RSM) is an important software design and analysis method. In the multi-factor level optimization experiments, the software is often used to design the experimental scheme and obtain the experimental data. The regression equation was used to fit the functional relationship between the factors and the response values, and the optimal process parameters were predicted. The advantage of the response surface method is that it can effectively solve the practical problem [45]. The random error of the experiment is fully considered and the complex unknown function relations are fitted by simple quadratic polynomial in a small region. Compared with other optimal design methods, such as single factor design and orthogonal design, the response surface method can analyze each experimental level continuously, and the orthogonal design method can only analyze isolated experimental points. Therefore, the response surface method will be used to design the experimental scheme and analyze the experimental results in this paper, which not only validates the rationality of the design, but also can understand the significance and interaction of the factor level, and predict the best process parameters.

3.3.2. Experimental Design and Results

As the tensile strength of the algae powder/LDPE composites can reach a relatively high level based on the PE-g-MAH single factor experiment, and the flexural properties of the composites are continuously improved in these experiments. Therefore, the flexural strength and flexural modulus of the composites are considered as the further research objects. Combined with the results of the single factor experiments, the three factors of the compatibilizer addition, lubricant addition, and plasticizer addition are selected for the investigation. The three-factor and three-level experiments are designed with the response values of the flexural strength and flexural modulus. The experimental factors and levels are shown in Table 2, and the experimental design and results are given in Table 3.

Table 2. The response surface design of the factors and levels.

Level	A: Compatibilizer (PE-g-MAH) Mass Ratio/wt%	B: Lubricant (PE-Wax and White Oil) Mass Ratio/wt%	C: Plasticizer (Glycerin) Mass Ratio/wt%
−1	1.00	1.33	2.00
0	3.00	2.67	3.00
1	5.00	4.00	4.00

Table 3. The response surface design of the experimental results.

Run	Factors			Flexural Strength/MPa	Flexural Modulus/MPa
	A	B	C		
1	−1	1	0	9.45	208.00
2	0	0	0	9.96	243.00
3	1	−1	0	9.71	219.00
4	−1	0	1	9.43	209.00
5	0	−1	1	9.31	206.00
6	−1	0	−1	8.90	179.00
7	1	0	1	9.45	206.00
8	0	1	1	8.96	190.00
9	0	0	0	9.95	242.00
10	0	1	−1	8.93	185.00
11	1	0	−1	9.31	202.00
12	0	−1	−1	8.86	173.00
13	−1	−1	0	9.48	209.00
14	0	0	0	9.82	242.00
15	0	0	0	9.92	243.00
16	1	1	0	9.72	220.00
17	0	0	0	9.90	241.00

3.3.3. Establishment and Variance Analysis of Multivariate Quadratic Response Surface Regression Model

The experimental results in Table 3 are fitted by the software Design Expert 8.0.6, the regression model equations for the response variables and response factors are as follow:

$$Y_{\mathrm{FS}} = 9.91 + 0.12A - 0.037B + 0.14C + 0.01AB - 0.098AC - 0.10BC - 0.031A^2 - 0.29B^2 - 0.61C^2, \quad (2)$$

$$Y_{\mathrm{FM}} = 242.20 + 5.25A - 0.50B + 9.00C + 0.50AB - 6.50AC - 7.00BC - 8.85A^2 - 19.35B^2 - 34.35C^2, \quad (3)$$

where Y_{FS} stands for flexural strength, Y_{FM} stands for flexural modulus, A stands for the addition of lubricant, B stands for the addition of PE-g-MAH, and C stands for the addition of glycerin. The obtained Equations (2) and (3) are analyzed for variance and the results are shown in Table 4.

Table 4. Regression equation of the variance analysis.

Source	Flexural Strength			Flexural Modulus		
	F-Value	*p*-Value	Significance	F-Value	*p*-Value	Significance
Model	71.16	<0.0001	**	925.64	<0.0001	**
A(compatibilizer)	29.14	0.0010	**	211.44	<0.0001	**
B(lubricant)	3.03	0.1252		1.92	0.2086	**
C(plasticizer)	44.55	0.0003	**	621.37	<0.0001	**
AB	0.11	0.7523		0.96	0.3601	
AC	10.25	0.0150	*	162.05	<0.0001	**
BC	11.88	0.0107	*	187.95	<0.0001	**
A^2	1.11	0.3275		316.23	<0.0001	**
B^2	94.61	<0.0001	**	1511.73	<0.0001	**
C^2	417.04	<0.0001	**	4763.93	<0.0001	**
Lack of FIT	1.46	0.3516		2.14	0.2376	
R^2		0.9892			0.9992	
$R^2_{(\mathrm{Adj})}$		0.9753			0.9981	
CV%		0.64			0.48	

Note: * Significant at $p < 0.05$. ** extremely significant at $p < 0.01$.

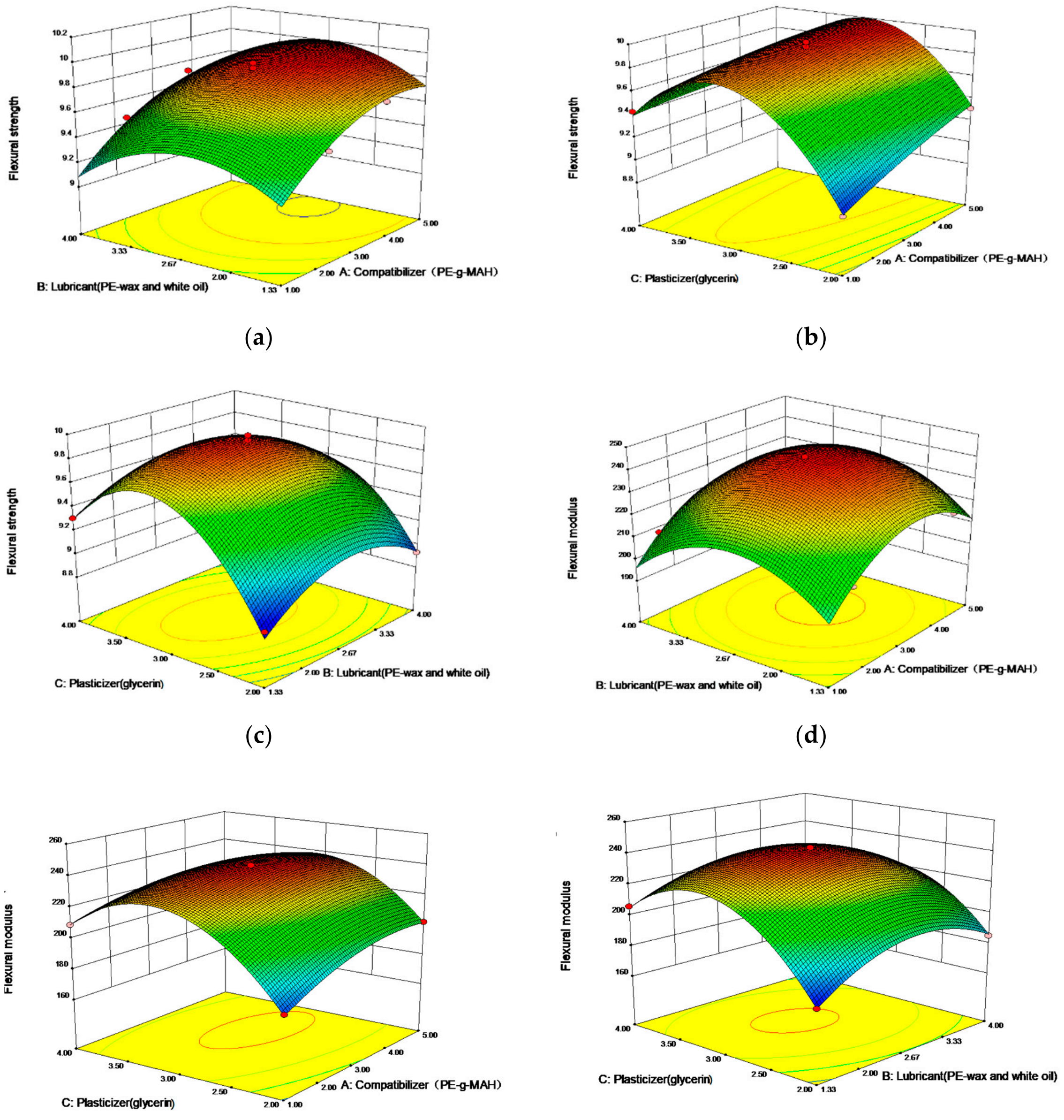
It can be seen from Table 4 that the model significance of the equation is $p < 0.0001$, which is extremely significant and indicates the model is meaningful [46]. The lack of FIT is $p > 0.05$, which is not significant and shows that the model is reasonable in the regression region and can be used to analyze and predict the experimental results of flexural strength and flexural modulus. The multivariate correlation coefficient R^2 is 0.9892 and 0.9992, and the correction coefficient $R^2{}_{Adj}$ is 0.9753 and 0.9981, respectively, which indicates that the model has a good fitting degree [47], and there is little difference between the model and the experimental values. The coefficient of variation is 0.64 and 0.48, indicating that the model had good repeatability, the experimental design is reasonable. Therefore, the experimental results can be predicted and analyzed using a regression equation.

It is known that the smaller the p value and the larger the F value of the response factor in the model, the more significant the effect of the response factor on the response variable [48]. It can be seen from Table 4 that the order of the effect of the three response factors on the flexural strength and flexural modulus is glycerin (C) > PE-g-MAH (A) > lubricant (B). In addition, the interaction among the three response factors is also characterized. AC and BC have a significant effect on the flexural properties, indicating that the interaction between PE-g-MAH and glycerin is obvious, the interaction between lubricant and glycerin is obvious too. While AB has no significant effect on the flexural properties, it shows that the interaction between the two groups of response factors is not obvious.

3.3.4. Response Surface Analysis

According to the shape of the response surface, the interactions between the PE-g-MAH, PE-wax/white oil, and glycerin on the flexural properties of the composites are analyzed, as shown in Figure 5.

As can be seen from Figure 5a,d, the contour lines on the XY plane are sparse and regular, and the slope of the response surface is steep when one of the influence factors changes, and flat when the other influence factor changes. The results indicate that there is no significant interaction between the two factors, indicating that there is no significant interaction between PE-g-MAH (A) and lubricant (B). In addition, in Figure 5b,e, the contour lines on the XY plane are dense and elliptical in shape, and the gradient of the response surface is relatively steep, which indicates that the PE-g-MAH (A) and glycerin (C) are not independent, and there is a certain interaction. This may be due to glycerin as a small molecular plasticizer intermolecular intercalation, not only in the molecular chain of the impact on the mobility of the molecular chain, it also affects the esterification reaction between biomolecules and PE-g-MAH. Finally, in Figure 5c,f, the response surface also shows a similar variation, indicating that lubricant (B) and glycerin (C) are not independent of each other and that there is some interaction between them. The possible reason is that glycerol as a plasticizer will also affect the compatibility of biomolecules with lubricants.



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 5. Combined effect of compatibilizer and lubricant (**a**,**d**), compatibilizer and plasticizer (**b**,**e**), lubricant and plasticizer (**c**,**f**) on flexural strength and flexural modulus, respectively.

3.3.5. Prediction and Verification of Optimal Experimental Conditions

With the software, the optimum conditions of factors leading to the maximized values of responses flexural strength and flexural modulus are obtained: the addition of compatibilizer, lubricant and plasticizer are 4.06, 2.61, and 3.08 wt%, respectively. Considering actual operating conditions, the parameters are revised to PE-g-MAH of 4.00 wt%, lubricant of 2.67 wt%, and glycerin of 3.00 wt%. Three experiments are conducted under the above conditions to verify the reliability of the response surface method.

Under this condition, the flexural strength and flexural modulus of algae powder/LDPE composites are 9.95 and 241.00 MPa, which are close to the predicted value of 9.96756 and 242.718 MPa, respectively. The results show that the model can better predict the optimization of the flexural properties of the composites. The tensile strength of the algae powder/LDPE composites is 11.60 MPa. Compared with the mechanical properties of the composites without additives, the mechanical properties of the obtained composites are greatly improved. As the composite particles prepared in this experiment are mainly used to produce EPE foam, film and hard packing boxes with special shapes. If the mechanical properties of the composite particles are improved, the properties of the products produced by them will also be improved. For example, the production of shopping bags or garbage bags will be able to withstand greater tension, the bending performance of the packaging box is enhanced, which is more suitable for protecting the fragile and fragile products. As a result, the products will be more competitive, and the application field will be wider.

3.4. Weight Loss Rate of Composite Film

The weight loss rate of the composite film is shown in Figure 6. As can be seen from the diagram, under the same conditions, LDPE film weight change is close to 0.10%, and there is substantially no change. The composite film prepared by this experiment has better degradation ability, and the weight loss rate can reach 7.73% at six months. The reason for this change may be that there are abundant microorganisms in the flowerpot soil, which distribute evenly in the early stage of the experiment. With the consumption of carbon and nitrogen sources in the soil, the microbes migrate and accumulate spontaneously. At this point, the biological components in the composite film become the main energy supply for the survival of microorganisms, and accelerate the rate of consumption. At the same time, the same composite film was left unfilled and placed directly in the room for 6 months, the appearance and weight did not changed significantly.

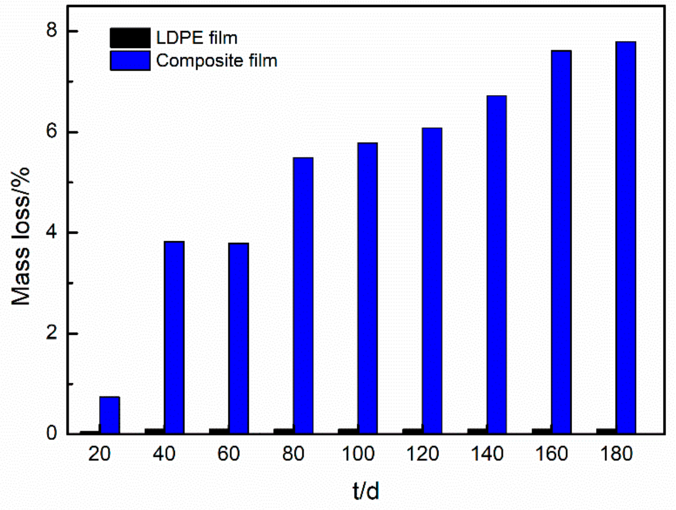


Figure 6. Mass loss of pure LDPE film and composite film embedded in soil.

4. Conclusions

The algae from Lake Chao could be used to combine with thermoplastic resin to prepare composite materials, and exhibited a better performance. In this paper, the response factors were determined by single factor experiments, the mechanical properties of composites are optimized by response surface method, and the regression model was analyzed by variance and response surface methodology.

During the experiment, the influence order of the three factors on the flexural properties of the composites was: glycerin > PE-g-MAH > lubricant (PE-wax and white oil), and the interaction between PE-g-MAH and lubricant was not significant, while the PE-g-MAH and glycerol, lubricant and glycerol had significant interaction. The optimum preparation conditions were found as follows: the addition of algae powder, LDPE, PE-g-MAH, lubricant and glycerol were 15.00, 85.00, 4.00, 2.67, and 3.00 wt%, respectively. The tensile strength, flexural strength and flexural modulus of the composites were 11.60, 9.95, and 241.00 MPa, respectively. At this time, the tensile strength of the composite decreased slightly, but the flexural strength increased greatly. And, which were 18.37%, 37.81%, and 43.45% higher than those of 9.80, 7.22, and 168.00 MPa without additives.

The composite not only has good mechanical properties, but also has good degradation properties. The six-month weight loss rate can reach 7.73%. So, we can speculate, through this low-cost method, the utilization of algae from Lake Chao can be realized, and the use of resin materials can also be reduced indirectly.

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