

Bioplastics and their Thermoplastic Blends from *Spirulina* and *Chlorella* Microalgae

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ABSTRACT: This research study focuses on the thermomechanical polymerization of microalgae protein biomass such as *Chlorella* and *Spirulina* to develop algal-based bioplastics and thermoplastic blends. The algal protein biomass can grow on nutrient-rich wastewater from livestock farms, municipal or industrial effluent sources, remediating the excess nitrogen and phosphorus. The algal bioplastics provide biodegradability that can be tailored to have a wide range of material properties suitable for various applications—consumable and disposable plastic products, agricultural plastic products, and horticultural planting containers. According to experimental results, pressure, temperature, content of plasticizer, and processing time are major variables in polymerization and structure stabilization during the compression molding process of both algal protein biomass and thermoplastic blends containing polyethylene polymer. *Chlorella* showed better bioplastic behavior than *Spirulina* microalgae, whereas *Spirulina* showed better blend performance.

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INTRODUCTION

Today's consumer needs materials that are inexpensive, versatile, and convenient in making plastics—a widely used material for many applications. Petroleum-based plastics, a major constituent of world plastic consumption, have production advantages from large economies of scale and mature technologies.¹ This consumption of plastics stems from their strength while keeping a low weight, resistance to degradation by water, chemicals, sunlight, and bacteria, as well as their capacity to provide electrical and thermal insulation. Although these features make conventional plastics suitable to many applications, they also come with environmental and economical concerns. Polystyrene is one of the widely used plastics, yet very slow to biodegrade in the environment. HIPS (High Impact Polystyrene), a copolymer of polystyrene and polybutadiene, is a low cost, easy to machine, and fabricate plastic materials. It has high-dimensional stability and impact resistance, and excellent machinability properties for low strength structural applications.² HIPS uses 99.8 GJ of energy to produce 1000 kg of resin, coming mostly from natural gas as the energy source.³ This resource consumption is further inflated because conventional plastics are produced from crude oil, an increasingly dwindling resource, as a chemical precursor in this energy costly process that yields HIPS resin.⁴ Beyond these consumption issues, the

process of resin production further harms the environment by producing waste products, leading to air, water, and ground contamination. Some of these waste products are known toxins that can leach out over time leading to ground water reservoir contamination.³ Further, the properties that make conventional plastics attractive for commercial applications also add environmental costs by preventing biodegradation, increasing demand and size of landfills to manage the increasing amounts of plastic entering the municipal solid waste stream. Therefore, there has been an increased focus on utilizing biodegradable components in the disposable and other consumer products (majority manufactured from polyethylene and polypropylene) to reduce dependence on petroleum materials^{5–7} and fixing the atmospheric CO₂.⁸ In this research study, we used polyethylene as a model polymer to develop and characterize thermoplastic blends with algae.

One solution to these problems is recycling plastics, which can reduce the filling of landfills, and thus leaching of chemicals by extending the use of a material; however, this has inherent energy consumption issues. A study of packaging materials produced from HIPS showed that 18.9 MJ of energy was required to produce 1 kg of recycled material, a cost that was about 23.5% the cost of producing the same product from virgin raw materials.⁹ Although recycling does dramatically reduce the

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environmental cost of producing virgin plastic materials, it also has its own environmental effects, and requires consumers to play an active role in producing sustainability. These problems allow conventional plastics no longer a sustainable solution in applications, such as packaging and short-term use products—in which large quantities of plastic materials are produced and disposed causing significant cost to our environments.

Bio-based plastics from natural feedstocks present a biodegradable alternative to conventional plastics, thereby significantly reducing environmental strain and the use of fossil fuel reserves. Currently, the carbohydrates fractions of biomass—starch and cellulose from corn, wheat, rice, and potato—have been used as base material for conversion into bio-based plastics, such as polylactic acid (PLA), cellulose acetate (CA), and thermoplastic starch (TPS). Another approach to forming bio-based plastics is to use natural protein biopolymers that have been thermomechanically processed.¹⁰ Many of these protein-based plastics studied come from terrestrial crops—soybean and sunflower seed.^{11,12} Of these crops, soybean, one of the most widely studied proteins, has been used for making bioplastic articles and films. Casein from milk protein also has a long history of use in making bioplastic articles and bio-based paints. A primary limitation of conventional bio-based plastics is that the biomass source competes with food and feed applications, and these agr crops consume large amounts of petroleum products in their life cycle. In addition, these terrestrial crops require large amounts of fertile land, irrigation water, and fertilizers and take time to grow in between harvest to produce the quantities of biomass required to replace conventional plastic feedstock markets.

In contrast to using conventional food staples for conversion into bioplastics, an alternative biomass has been identified in microalgae. These small aquatic organisms consist of high-protein compositions, with *Spirulina* ranging from 46% to 63% protein in dry weight, and *Chlorella* ranging from 51% to 58% protein in dry weight.¹³ Furthermore, both *Chlorella* and *Spirulina* have fairly small cell sizes, lending them to be more useful in fiber and film market in which particle size is limiting. These microalgae's small size and high-protein composition also allow them to be suitable for plastic conversion without any prior treatment, making scalable production more cost-effective and reducing waste production. Besides, these microalgae have well studied and understood production methods because they are commonly produced in scale for nutraceutical application. Both of these microalgae can be used for wastewater remediation for the removal of nitrogenous waste, which would only increase their protein production capacity. In addition, using wastewater as algae growth media, these algae production models are more suitable than conventional food crops, because they remediate water for further use, and can be grown in urban environments or on nonarable land, which would not be suitable for conventional food crop production. These species of microalgae also further serve the purpose of waste remediation and recycling by consuming CO₂ bubbled into the growth media to improve biomass production rates.¹⁴ Therefore, microalgae present an interesting opportunity to improve the sustainability of plastic production, and improving water supplies during production.

Overall, the objective of this research was to study the potential of high-proteinaceous microalgae in developing the bioplastics and thermoplastic blends that can be the viable and sustainable source for replacing or complementing the traditional, petroleum-based plastics.

EXPERIMENTAL

Materials

Microalgal biomass species *Chlorella vulgaris* (CV) and *Spirulina platensis* (SP) were used to determine their potential for bioplastic and thermoplastic blend production. The *Chlorella* species is a green alga typically found in freshwater environments and the *Spirulina* species is a cyanobacteria typically found in high-alkaline freshwater conditions; both of which are currently used in nutraceuticals industry. Microalgae biomass was sourced from nutraceutical sales company, nutsonline.com. According to company's compositional information, *Spirulina* consists of 57% protein and *Chlorella* of 58% protein. Ultra High Molecular Weight Polyethylene powder was received from Sigma Aldrich, USA and has particle sizes of 53–75 μm with a melting temperature of 144°C. Glycerol was also obtained from Sigma Aldrich with a purity of $\geq 99\%$.

Preparation of Plastic Samples

Thermomechanical molding of microalgae and hybrid blends was performed on a 24-ton bench-top press (Carver Model 3850, Wabash, IN, USA) with electrically heated and water-cooled platens, as described in our previous study.¹⁵ The stainless steel molds were custom made to form either a single dogbone or two small rectangular flexbars for DMA analysis. All data presented in this contribution were generated from compression molded samples using a 20 min cook time at 150°C followed by a 10 min cooling period. The 100% algae-based bioplastics and the thermoplastic blends of microalgae, polyethylene and glycerol, were made in small batches of 5 g by hand-mixing and then manually filled into the mold cavity to a standard weight, that is, 1.5 g for DMA flexbars and 5.0 g for dogbones using an Ohaus Precision Standard balance. Each formulation of microalgae and glycerol was thoroughly blended and then polyethylene was added for hybrid materials followed by further mixing. After the samples were cooled for 10 min under pressure, the pressure was released and the samples were removed. Figure 3 shows samples of compression molded dogbone (top) and DMA flexbar (bottom) used.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed on a DMA 8000 Dynamic Mechanical Analyzer from Perkin Elmer for specimens of 9 mm (width) \times 2.5 mm (thickness) \times 12.5 mm (length) using a dual-cantilever setup at a frequency of 1 Hz. All samples were run with a displacement of 0.05 mm from room temperature to 160°C at a temperature ramp of 2°C/min. All samples were run in double to ensure accuracy in measures.

Thermal Analysis

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC821e. TGA was performed from 25°C to 800°C under N₂ gas with a

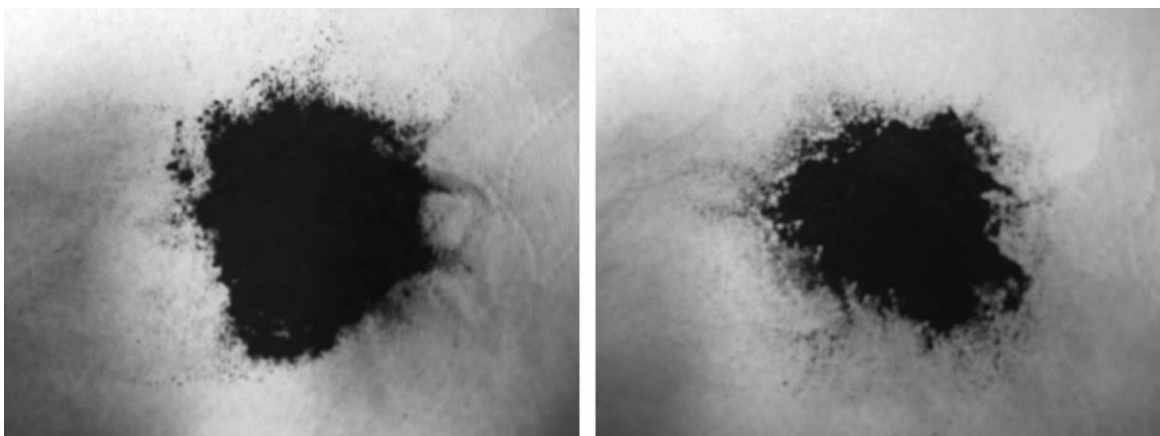


Figure 1. *Spirulina* and *Chlorella* raw biomass (*Spirulina* on left/*Chlorella* on right).

heating rate of 10°C/min. DSC was performed from -50°C to 250°C under N₂ gas with a heating rate of 20°C/min. All samples were prepared with sample weights between 4 and 10 mg, and plastic samples were cut from DMA flexbar-molded plastic materials.

Scanning Electron Microscopy

Samples were made from cryogenic DMA flexbar fracture surfaces. DMA flexbars were immersed in liquid nitrogen for 20 s after which they were immediately broken. All samples were prepared by mounting and then sputter coating for 60 s with an Au/Pt mix. SEM images were recorded on a Zeiss 1450EP variable pressure scanning electron microscope (SEM). Coated samples were analyzed at 20×, 100×, 500×, and 1000× for plastic fracture samples and 100×, 500×, and 3000× for raw biomass samples.

Mechanical Properties

Tensile properties such as stress and extension at maximum load were measured using the Instron testing system (Model 3343) interfaced with computer operating Blue Hill software. The test was performed under a controlled environment (20°C; 65% RH), according to the standard test method for tensile properties of plastics (ASTM D638-86) at 5 mm min⁻¹ cross-head speed with a static load cell of 1000 N and a gauge length of 60 mm using dogbone specimens (distance between clamps or gauge length of 60 mm, thickness of 2.5 mm, and width of 14.5 mm). The specimens were conditioned at standard conditions (20°C; 65% RH) for 24 h before testing and were run in quintuplicates.

RESULTS AND DISCUSSION

Material Analysis of Algae

Figure 1 shows raw microalgal biomass and Figure 2 shows SEM pictures for chosen microalgal species such as *CV* and *SP* algae. As designated by the supplier, both *SP* and *CV* consist of 58% protein by weight. As seen in SEM micrographs in Figure 2, *Chlorella* and *Spirulina* both have relatively small cell sizes being in general less than 50 μm. This reduced cell size contributes to a better dispersion in the matrix when blended with polyolefins, making these algal biomasses more suitable for fiber and film applications in which particle size is an important criterion. In

addition, in Figure 1(b) helical structure of native cells can be recognized after desiccation in smaller cells. Figure 3 shows compression-molded *Spirulina* and *Chlorella* samples used for testing.

TGA and DSC of *Spirulina* and *Chlorella* biomass are represented in Figure 4. *Spirulina* shows a two-step degradation. The

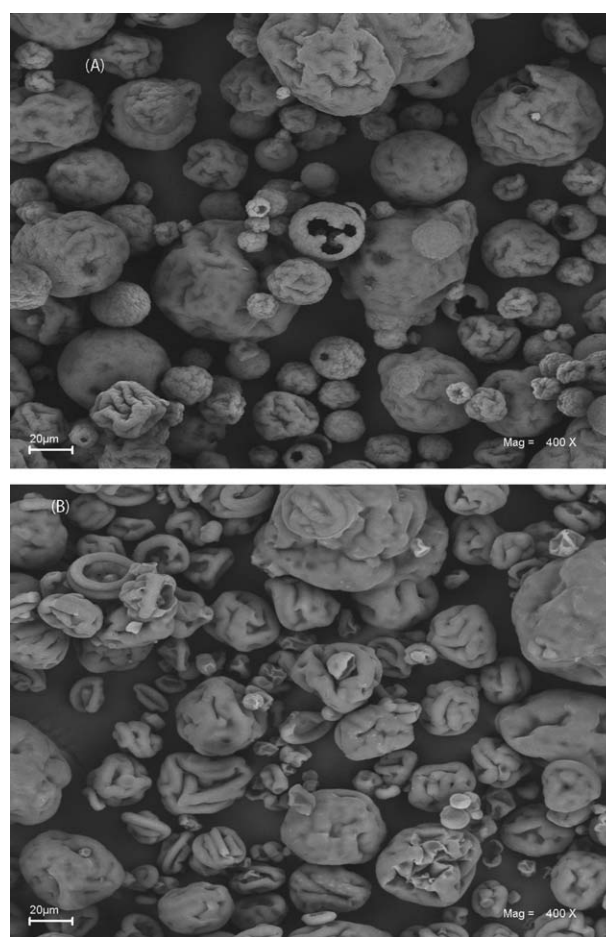


Figure 2. SEM micrographs of microalgae such as A. (*Chlorella*) and B. (*Spirulina*).

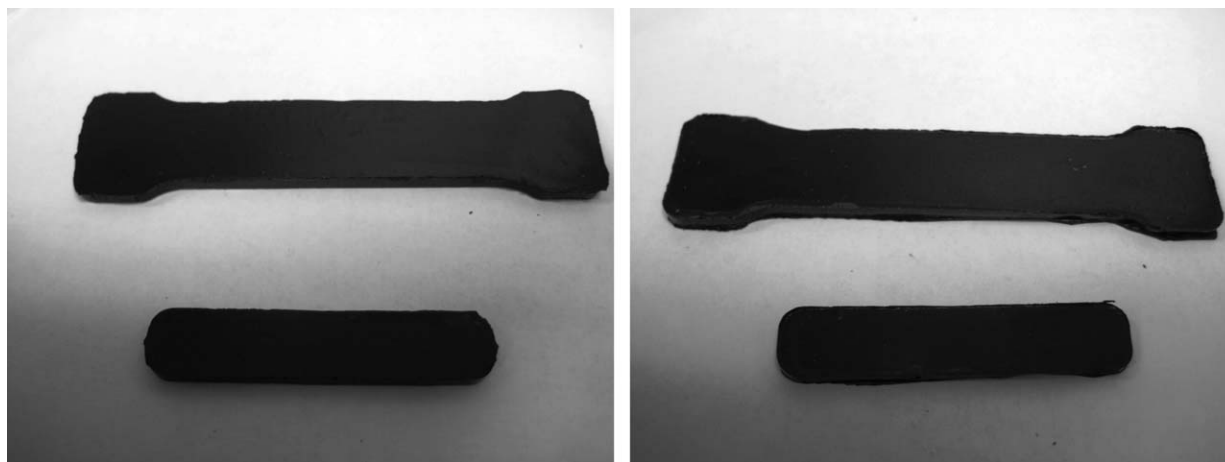


Figure 3. *Spirulina* and *Chlorella* compression-molded samples (*Spirulina* on left/*Chlorella* on right).

first degradation starting at about 30°C and ending at about 130°C representing the bound water and low volatile loss and the second starting at about 200°C and ending at about 370°C, which is likely representative of carbohydrate and protein degradation. *Chlorella* has a three-step degradation. The first degradation being the same water evaporation seen in *Spirulina* from 30°C to 130°C, *Chlorella*'s second degradation is similar to *Spirulina* as well beginning at 200°C, and the third degradation represented by a shoulder from 300°C to 375°C obscures the end of this degradation. The second degradation and third degradation are both likely because of carbohydrate and protein degradation with some distinction between thermally sensitive components and thermally resistant components resulting in the bimodal peak demonstrated because they occur in the range where carbohydrates are typically degraded.¹⁶ Moreover, the bimodal degradation behavior may be attributed to the presence of higher amount of network amino acid, cysteine¹³ in *Chlorella* alga.

DSC of both *Spirulina* and *Chlorella* show denaturation peaks that begin at 40°C and end at 170°C, with the main difference between the two being *Spirulina* having a peak denaturation at about 100°C and *Chlorella* having a peak denaturation at about 110°C. These DSC results indicate that proteins are maximally denatured by 170°C; however, TGA results indicate that degradation can occur as early as 175°C. This means, both biomasses should be processed at 150°C because this is the highest temperature possible without risking degradation, while still yielding maximum denaturation.

Thermal Analysis of Bioplastics

Figure 5 shows the TGA of *Spirulina* and *Chlorella* bioplastics. The amount of glycerol was varied from 0% to 30% (by weight) to determine most suitable plasticization ratio of protein and plasticizer. The degradation of plasticized SP bioplastics consisted of two weight loss steps. The first gradual weight loss (between 150°C and 200°C) is because of the glycerol evaporation and the second weight loss beyond 200°C can be attributed to the decomposition of SP proteinaceous materials.¹⁷ *Spirulina* bioplastics show one degradation peak at about 290°C for all formulations. This degradation was left shifted in bioplastics

with more glycerol making the start of this degradation variable from 200°C to 225°C; however, the maximum or peak degradation remained consistent indicating that the addition of glycerol aided in degradation and allowed it to occur at lower temperatures. Lowering of the degradation temperature is likely the

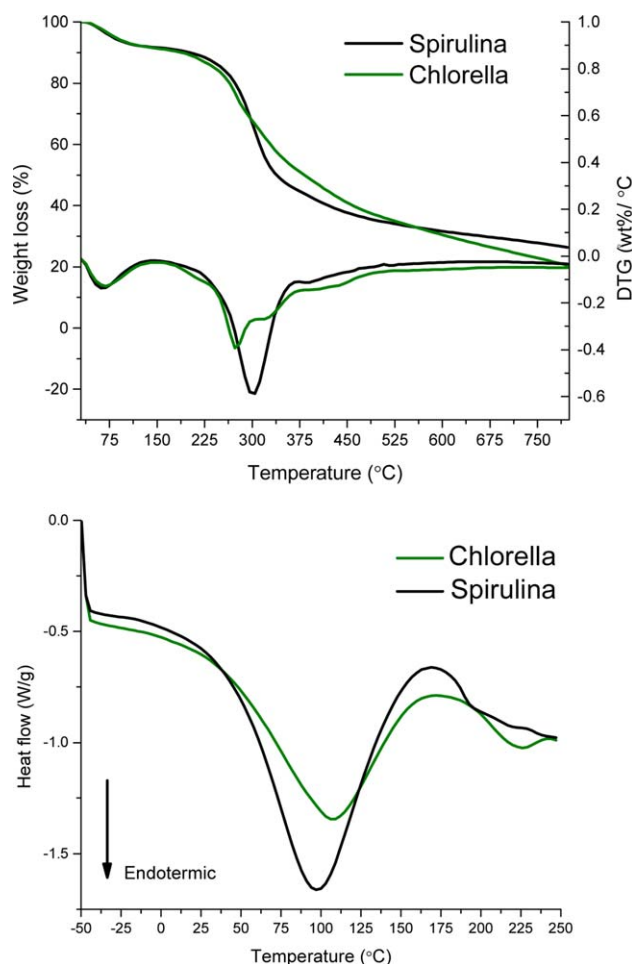


Figure 4. TGA and DSC of algal biomass. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

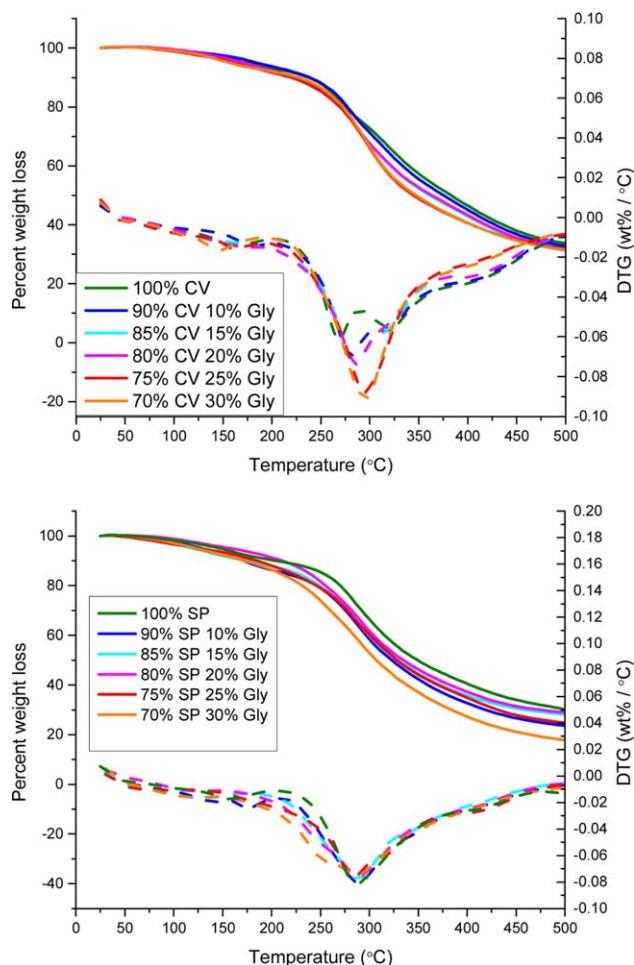


Figure 5. TGA of *Spirulina* and *Chlorella* bioplastics at various proportion of glycerol. Note: SP stands for *Spirulina platensis* whereas CV for *Chlorella vulgaris* microalgae. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result of glycerol interfering with interactions between carbohydrate and protein molecules in the plastic matrix, and making these macromolecules more available for degradation.

For *Chlorella* bioplastics, a bimodal peak is seen in formulations with less glycerol and eventually becomes a single peak in formulations with most glycerol. This bimodal-to-single peak transition results from the second degradation in the bimodal peak becoming more left shifted, creating the single peak. This transition again demonstrates how glycerol interferes with macromolecule interactions and allows degradation to occur earlier. The *Chlorella* formulations with less glycerol also showed a slight degradation from about 350°C to 475°C, which shows a stable component (carbonaceous residue from carbohydrate) to these plastics that resists thermal decomposition. In addition, nearly all the *Chlorella* bioplastics demonstrated a slight peak at about 180°C, which is likely a product of glycerol degradation.

Figure 6 shows the DSC for *Spirulina* and *Chlorella* bioplastics. In *Chlorella* bioplastics, a peak at 175°C may be attributed to onset of degradation, and is more obvious in less plasticized samples. In less plasticized samples, a glass transition can be

seen for *Chlorella* starting at about 40°C for 100% and 90% *Chlorella* formulations, suggesting antiplasticizing effect¹⁸; however, the glass transition is lost with increasing plasticizer use, suggesting that it leads to less plastic-like characteristics or plasticizing effect. With high degree of plasticization (in this case, increase in the content of glycerol plasticizer), protein–protein interactions are mostly replaced with protein–plasticizer interactions, not allowing protein macromolecules to produce structuration (beta-sheets, etc.), therefore loosing plastic-like characteristics. While *Spirulina*'s potential degradation peaks are seen as well for less-plasticized samples at about 165°C, they are lost as more plasticizer is added. Therefore, for *Chlorella* and *Spirulina* lower plasticization is required to maintain a plastic state. For *Spirulina*, anything above 25% glycerol would be questionable, and above 25% glycerol for *Chlorella* is also not recommended because of small size of the melting peaks.

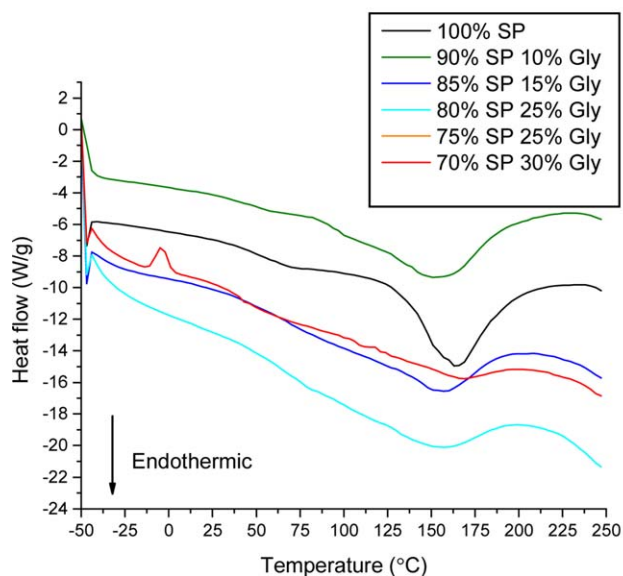
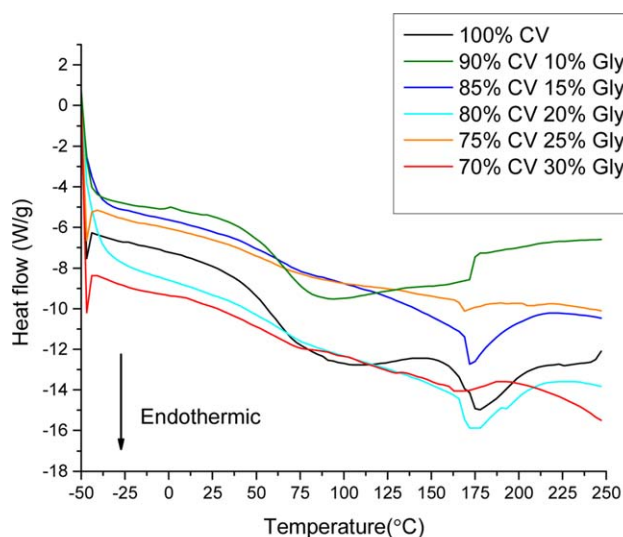


Figure 6. DSC for *Spirulina* and *Chlorella* bioplastics at various proportion of glycerol. Note: SP stands for *Spirulina platensis* whereas CV for *Chlorella vulgaris* microalgae. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

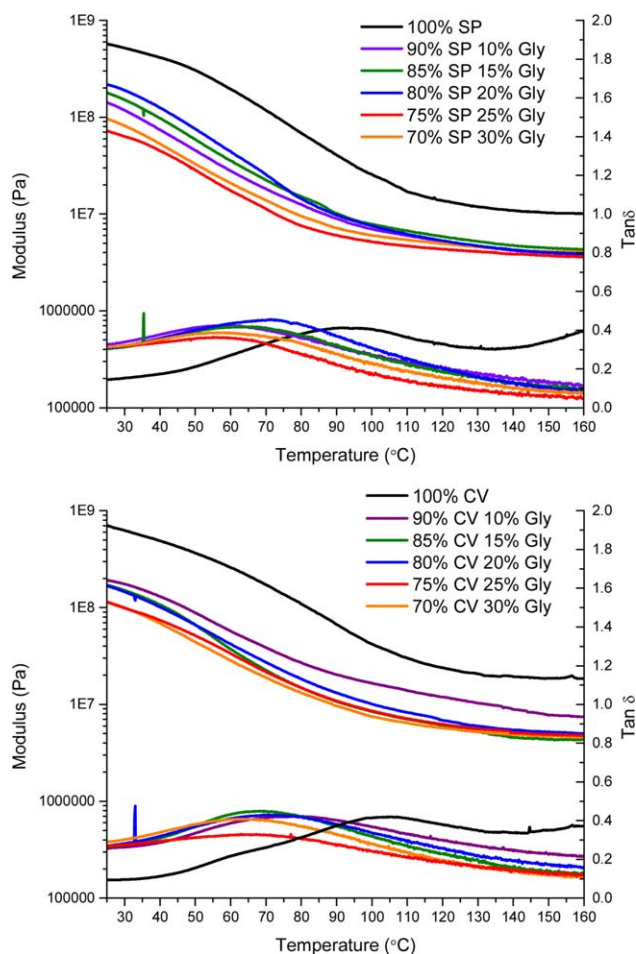


Figure 7. DMA of *Spirulina* and *Chlorella* bioplastics at various proportion of glycerol. Note: SP stands for *Spirulina platensis* whereas CV for *Chlorella vulgaris* microalgae. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic Mechanical Analysis

Figure 7 shows DMA of *Spirulina* and *Chlorella* bioplastics. *Spirulina* bioplastics showed consistent Tan Delta and modulus values for all plasticized bioplastics, with a significant change with increasing plasticization. As glycerol levels rise, so does the modulus, and tan delta with a shift to higher temperatures until 80% SP 20% Gly, in which the trend reverses with increased glycerol resulting in lower modulus and lower tan delta with lower temperature peaks. This shift shows that the 80% SP 20% Gly formulation is most stable and desirable formulation for material properties. The *Chlorella* formulations 90% CV 10% Gly has the highest modulus values, but has lower and more right shifted tan delta values. The second highest modulus values are seen in 80% CV 20% Gly and it also has second highest tan delta at all points before about 90°C. The highest tan delta values are seen in 70% CV 30% Gly before about 50°C, in 85% CV 15% Gly from about 50°C to 90°C, and in 100% CV from 90°C and above. Bioplastics, plasticized with glycerol, exhibit the well-known transition from glassy to rubbery region, with a peak in tan delta close to 70°C.¹⁹ Because there is no clear best formulation for *Chlorella* bioplastics, 80% CV 20% Gly was considered the best because it maintained high modulus while

still keeping a comparatively high tan delta and a good left shift compared to other bioplastics in DMA testing.

Because of the performance of 80% CV/20% glycerol and 80%SP/20% glycerol formulations, a ratio of 1:4 glycerol to algae was used to determine the glycerol quantity needed for hybrid algae/polyolefin blends. The quantity of glycerol needed to plasticize a quantity of algae in blends was determined by eq. (1).¹⁶

The carrying capacity of polyethylene for glycerol was 1/13.33 ratio of glycerol to polyethylene (results not shown), and the ratio of glycerol to microalgal of 1/4, as shown above, represents the preferred plasticization in an 80/20 ratio. Thermoplastic blends with 20%, 35%, 50%, 65%, and 80% polyethylene were made for DMA analysis, and the amount of glycerol and microalgae needed for formulations was determined by using eq. (1).

$$\text{Quantity of glycerol} = (\text{Grams of polyethylene})(1/13.3) + (\text{Grams of microalgae})(1/4) \quad (1)$$

Thermal Analysis of Thermoplastic Blends

Figure 8 shows TGA of *Spirulina* and *Chlorella* thermoplastic blends after blending with polyethylene. The *Chlorella* and

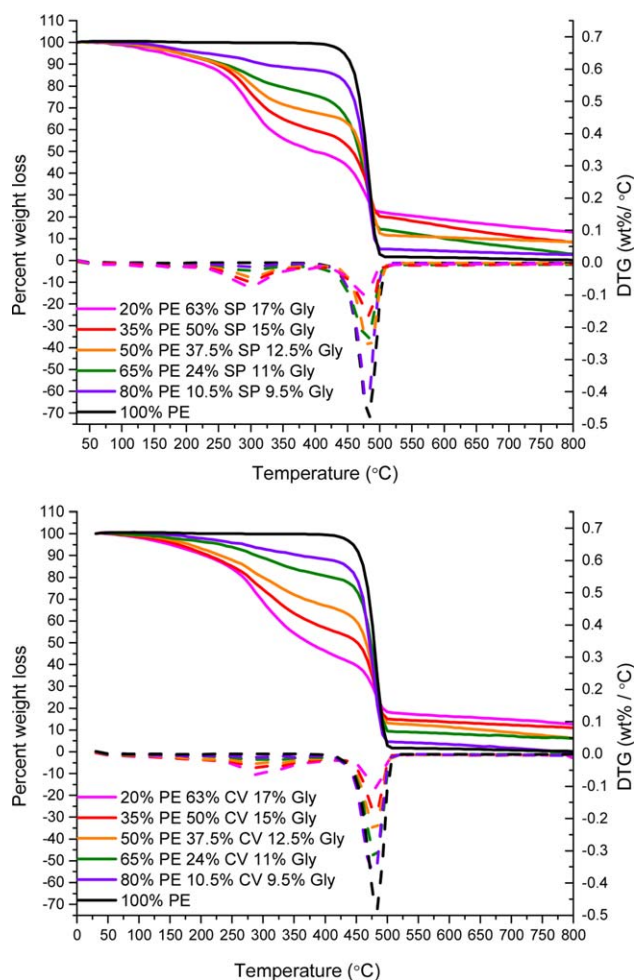


Figure 8. TGA of thermoplastic blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

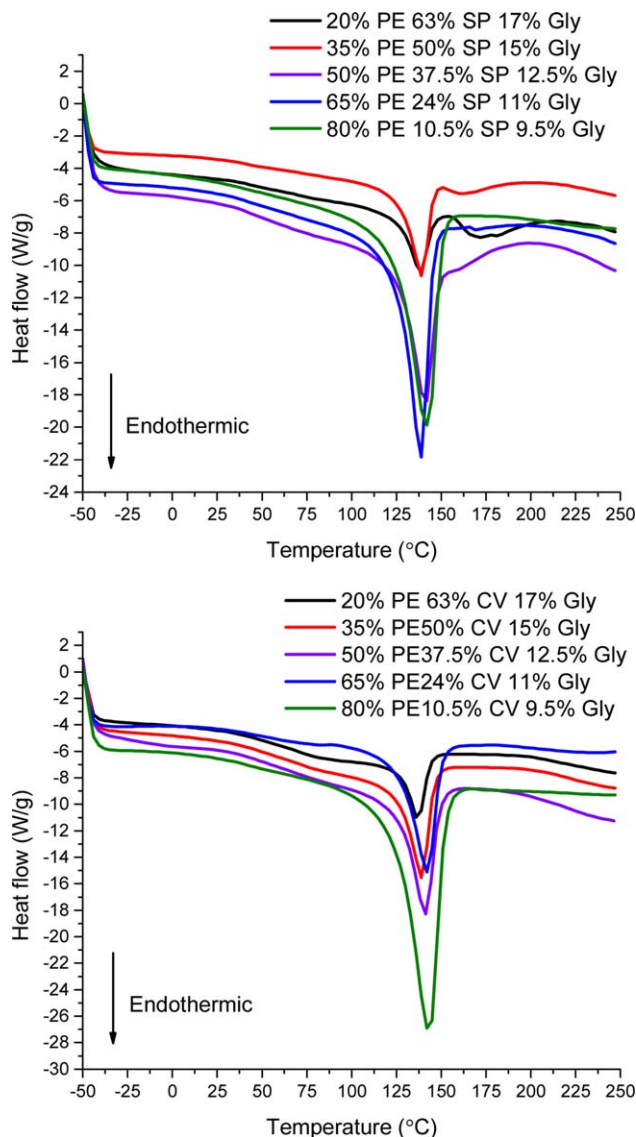


Figure 9. DSC data for *Spirulina* and *Chlorella* thermoplastic blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Spirulina thermoplastic blends both show polyethylene degradation peaks around 480°C. Both *Spirulina* and *Chlorella* degradation is shown in thermoplastic blends occurring between 225°C and 375°C for *Spirulina* and between 250°C and 400°C for *Chlorella*, with a maximum thermal decomposition at 300°C and 325°C, respectively. Corradini et al.,²¹ in a study on lignocellulosic fiber-reinforced starch/gluten/glycerol polymer matrix, also observed a maximum thermal decomposition temperature of 280°C because of gluten/starch components. In addition, worth mentioning is the loss of *Chlorella*'s multistep degradation, with just one discernible step for *Chlorella* degradation. However, this is likely caused by polyethylene's shielding effect on *Chlorella*. This effect from polyethylene could have effectively shifted the first degradation step back to align with the second degradation, making one degradation step visible.

Figure 9 shows DSC data for *Spirulina* and *Chlorella* thermoplastic blends. Both *Spirulina* and *Chlorella* blends have melting

points for polyethylene at around 130°C with increasing polyethylene percentage increasing the size of this peak. Also at about 40°C a possible glass transition in *Chlorella* blends can be observed, specifically in blends with a higher *Chlorella* percentage, likely a remnant of glass transitions seen in *Chlorella* bio-plastics. However, this transition is not readily clear in *Spirulina* blends, if it exists. *Spirulina* also shows a small dip after polyethylene melting in the higher percentage *Spirulina* formations, which may be a result of *Spirulina* degradation that can begin to occur after the polyethylene matrix is removed.

Dynamic Mechanical Analysis of Thermoplastic Blends

Figure 10 shows DMA of *Spirulina* and *Chlorella* thermoplastic blends. For both *Spirulina* and *Chlorella*, a shift of peak tan delta to higher temperature is observed as well as increasing modulus with higher polyethylene content. These variations may be attributed following interactions between blend-forming polymers and between the polymers and glycerol.²¹ SP and CV have higher tan delta values (height of tan delta peak) before 100°C with higher bio-based polymer content, but above 100°C

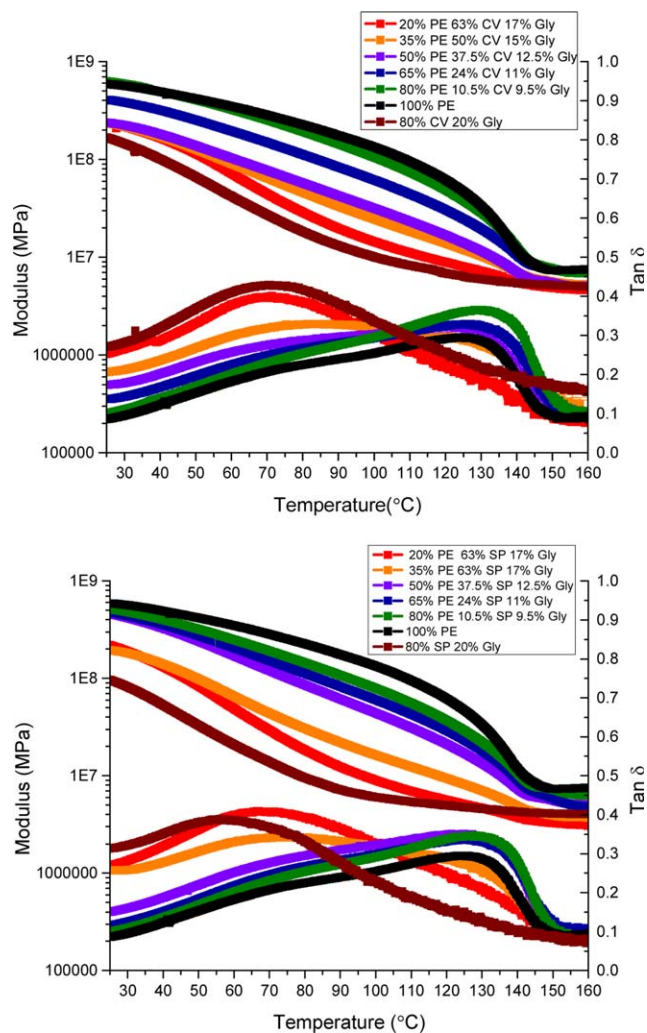


Figure 10. DMA of thermoplastic blends of *Spirulina* and *Chlorella*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tan delta is higher for samples that contain more polyethylene. This shows the bioplastic behavior of *SP* and *CV* at lower polyethylene content. Bioplastics, plasticized with glycerol, exhibit the well-known transition from glassy to rubbery region, with a

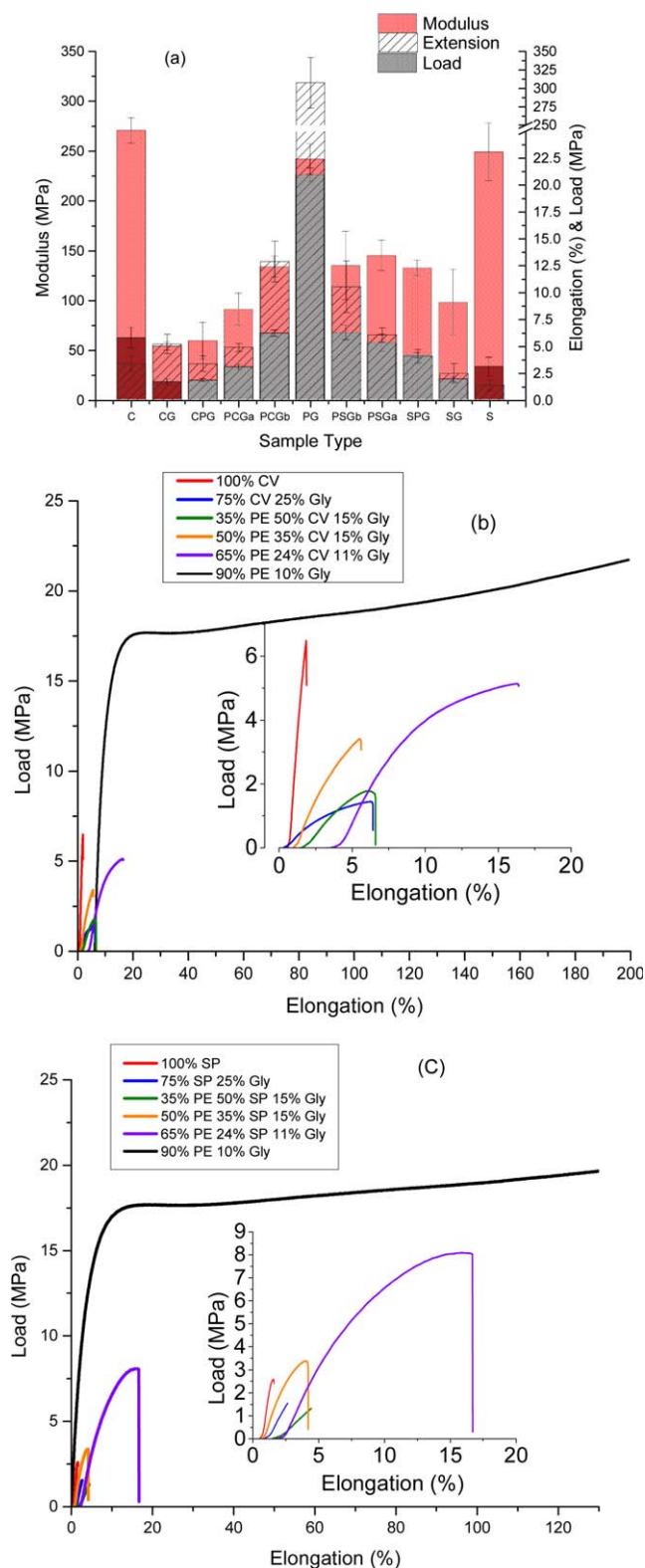


Figure 11.

Table 1. Comparison of Mechanical Properties of CV- and SP-Based Bioplastics to Other Bioplastics (Materials Labeled as Plasticized have Some Concentration of Glycerol, and All Materials are Compression Molded Bioplastics in Either a Thick Film or Dogbone Shape)

Bioplastic type	Percent extension	Stress (MPa)	Modulus (MPa)
Feather meal	1.4	9.2	-
Soy protein isolate	1.2	13.0	-
Duckweed	2.1	6.9	459
Plasticized duckweed	3.4	1.7	84
<i>Chlorella vulgaris</i>	3.4	5.7	270
Plasticized <i>Chlorella vulgaris</i>	5.2	1.6	53
<i>Spirulina platensis</i>	1.4	3.0	249
Plasticized <i>Spirulina platensis</i>	2.5	1.9	98

peak in tan delta close to 70°C.²⁰ Furthermore, for both *Spirulina* and *Chlorella*, a blending ratio at 80% polyethylene gives similar modulus values and higher tan delta values than 100% polyethylene samples. *Spirulina* shows significantly higher blend properties at 50% and 65% polyethylene ratios than *Chlorella*, likely because of improved interaction between polyethylene and *Spirulina*—the presence of more, hydrophobic, nonpolar amino acids.¹³ However, *Chlorella* performs better at polyethylene content of 20%, 35%, or 80% possibly because of *Chlorella* being a better bioplastic. Therefore, in blends where bioplastic is the predominant phase, *Chlorella* performs better, and at 80% it is better because it constitutes such a small fraction of blend that it behaves like a filler rather than separate phase, so its improved bioplastic properties make it perform better as a filler.

Mechanical Properties of Microalgal Plastics

Figure 11 shows the tensile properties for both *Spirulina* and *Chlorella* bioplastics and thermoplastic blends. Moreover, the first and most obvious conclusion from this data is that *Spirulina* is better as a thermoplastic blend, but *Chlorella* is a better bioplastic. This is seen because 100% CV has better load and extension than 100% *Spirulina* and 80:20 CV/Gly has better extension than 80:20% SP/Gly bioplastics.

Table 1 shows the comparison of SP and CV bioplastics with other bioplastic examples from the literatures that have a similar formulation. These bioplastics behave similar to soy protein isolate, duckweed, and feather meal bioplastics.¹⁵

However, when looking at thermoplastic blends, *Spirulina* is better in every category except extension in 65% polyethylene/35%

Figure 11. Tensile properties of *Spirulina* and *Chlorella* bioplastics and thermoplastic blends. (a) Mechanical performance values, (b) Stress-strain curves for CV, (c) Stress-strain curves for SP. Note: C = 100% CV, CG = 80:20 CV/Gly, CPG = 35:50:15 PE/CV/Gly, PCGa = 50:37.5:12.5 PE/CV/Gly, PCGb = 65:24:11 PE/CV/Gly, PG = 90:10 PE/Gly, PSGb = 65:24:11 PE/SP/Gly, PSGa = 50:37.5:12.5 PE/SP/Gly, SPG = 35:50:15 PE/SP/Gly, SG = 80:20 SP/Gly, and S = 100% SP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

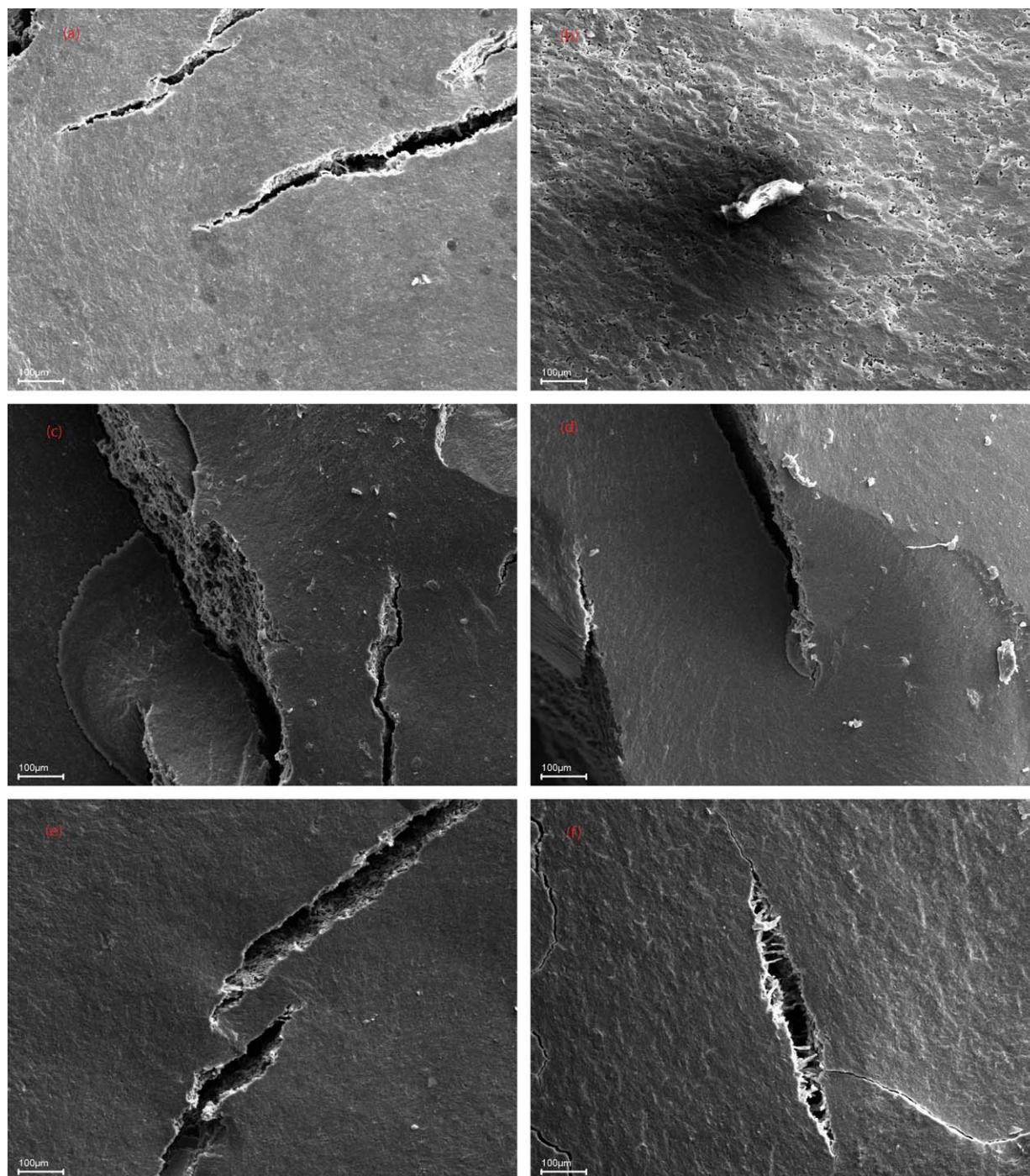


Figure 12. *Spirulina* bioplastic SEM (100 \times). (a) 70% SP 30% Gly, (b) 75% SP 25% Gly, (c) 80% SP 20% Gly, (d) 85% SP 15% Gly, (e) 90% SP 10% Gly, (f) 100% SP.

bio-blends. In addition, these 65% polyethylene/35% bio-blends have almost identical properties apart from extension, so it is likely that, at 65% PE blending ratio, the properties of the material are mainly determined by the polyethylene phase with extension being variable within a wide range. This may be because of *Spirulina* and *Chlorella* fractions not having a continuous phase in 65% polyethylene formulations resulting in no contribution to overall matrix stability from microalgal plastic phases. This proposed lack of continuity throughout the polymer matrix would

mean that at 65% polyethylene and higher, the microalgal fraction will act more like a filler. In addition, it seems that there may be some negative interactions between *Chlorella* and polyethylene phases because in transitioning from 80:20 CV/Gly to 35:50:15 PE/CV/Gly the extension actually decreased, and the load and modulus only slightly increased. Figure 11(b and c) shows the stress–strain curves for both thermoplastic blends and 100% bioplastics. It is obvious that 100% CV and SP bioplastics behave more like a brittle material. However, plasticized CV bioplastic

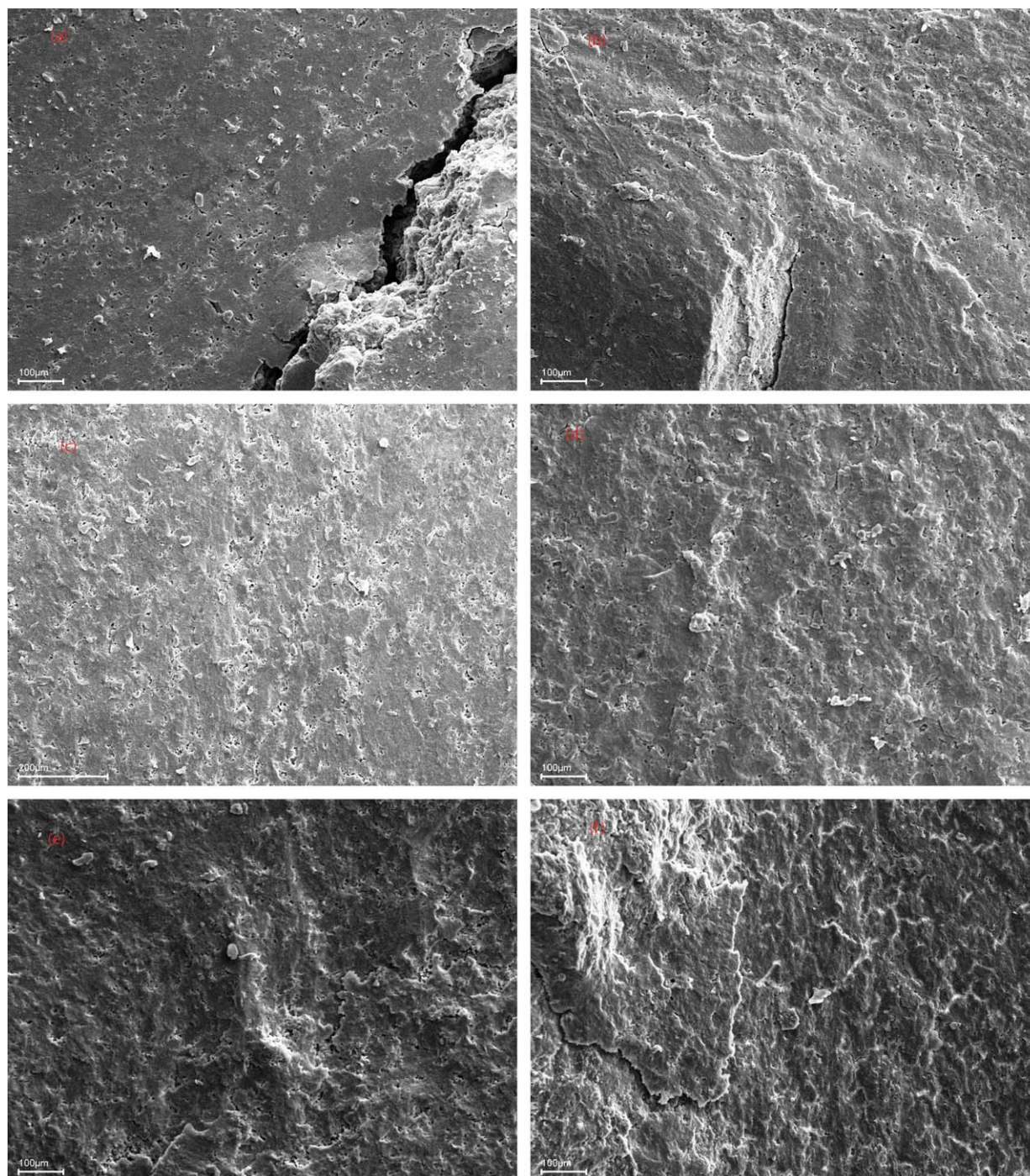


Figure 13. *Chlorella* bioplastics SEM (100 \times). (a) 70% CV 30% Gly, (b) 75% CV 25% Gly, (c) 80% CV 20% Gly, (d) 85% CV 15% Gly, (e) 90% CV 10% Gly, (f) 100% CV.

exhibits better plastic behavior (e.g., initial modulus and yielding) than plasticized *SP* bioplastics.

Because polyethylene is a small proportion and likely can not create its own continuous phase network, it must interact with *Chlorella* in order to yield positive benefits acting like a glue in a *Chlorella* matrix. However, because positive benefits are not observed and only negative effects can be seen, it can be deduced that polyethylene must have very weak interactions

with *Chlorella* bioplastics, which explains the phenomena of *Spirulina* having superior blends. This may be explained by the differing ratios of nonpolar amino acids to polar amino acids in the two algal specimens, with *Spirulina* having a ratio of 0.863, and *Chlorella* containing a ratio of 0.676.¹³ However, these amino acid ratio differences are likely not the only factors involved in determining the stability of polyethylene and algae phase interactions, and the differences between

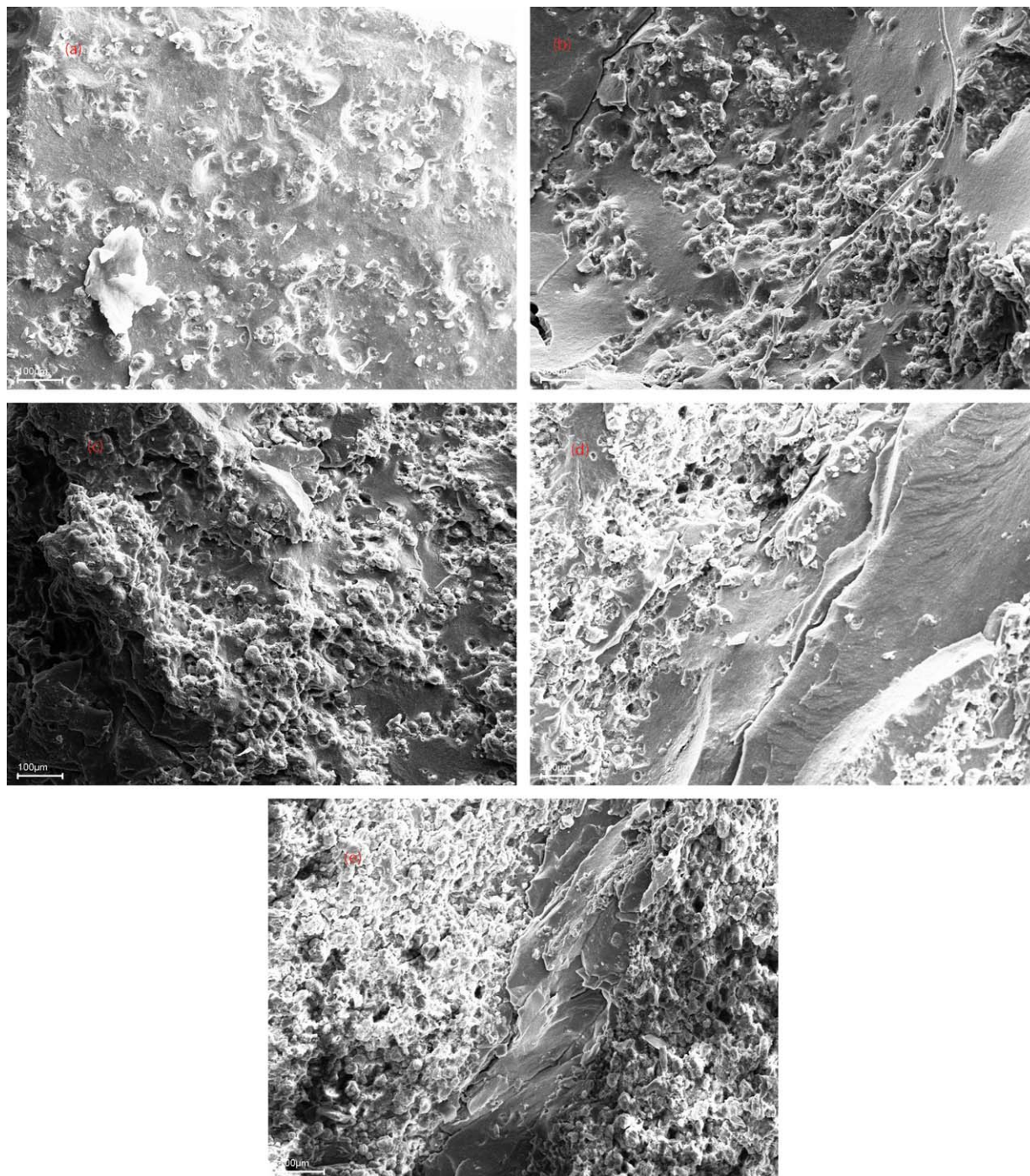


Figure 14. *Spirulina* thermoplastic blends SEM (100 \times). (a) 20% PE 63% SP 17% Gly, (b) 35% PE 50% SP 15% Gly, (c) 50% PE 37.5% SP 12.5% Gly, (d) 65% PE 24% SP 11% Gly, (e) 80% PE 10.5% SP 9.5% Gly.

Spirulina and *Chlorella* may be greater than just amino acid compositions.

***Spirulina* and *Chlorella* Bioplastics SEM**

Figures 12 and 13 show morphology of fracture surfaces for all plasticized *Spirulina* and *Chlorella* bioplastic. In Figure 12, very little change is seen in the overall topography of the *Spirulina* plastics, except in the case of 80/20 and 85/15 *Spirulina*/glycerol

blends, in which the texture of the surface is similar to other *Spirulina* bioplastics, but the bioplastics have large ridges instead to the flat surface on the other formulations. This may indicate more toughness in the material because toughness increases the rough nature of the break. However, there is no evidence of protein aggregates as observed by Corradini et al.²¹ with 20% glycerol-plasticized corn gluten meal (CGM). Figure 13 shows SEM images of fracture surfaces for *Chlorella* bioplastics for all

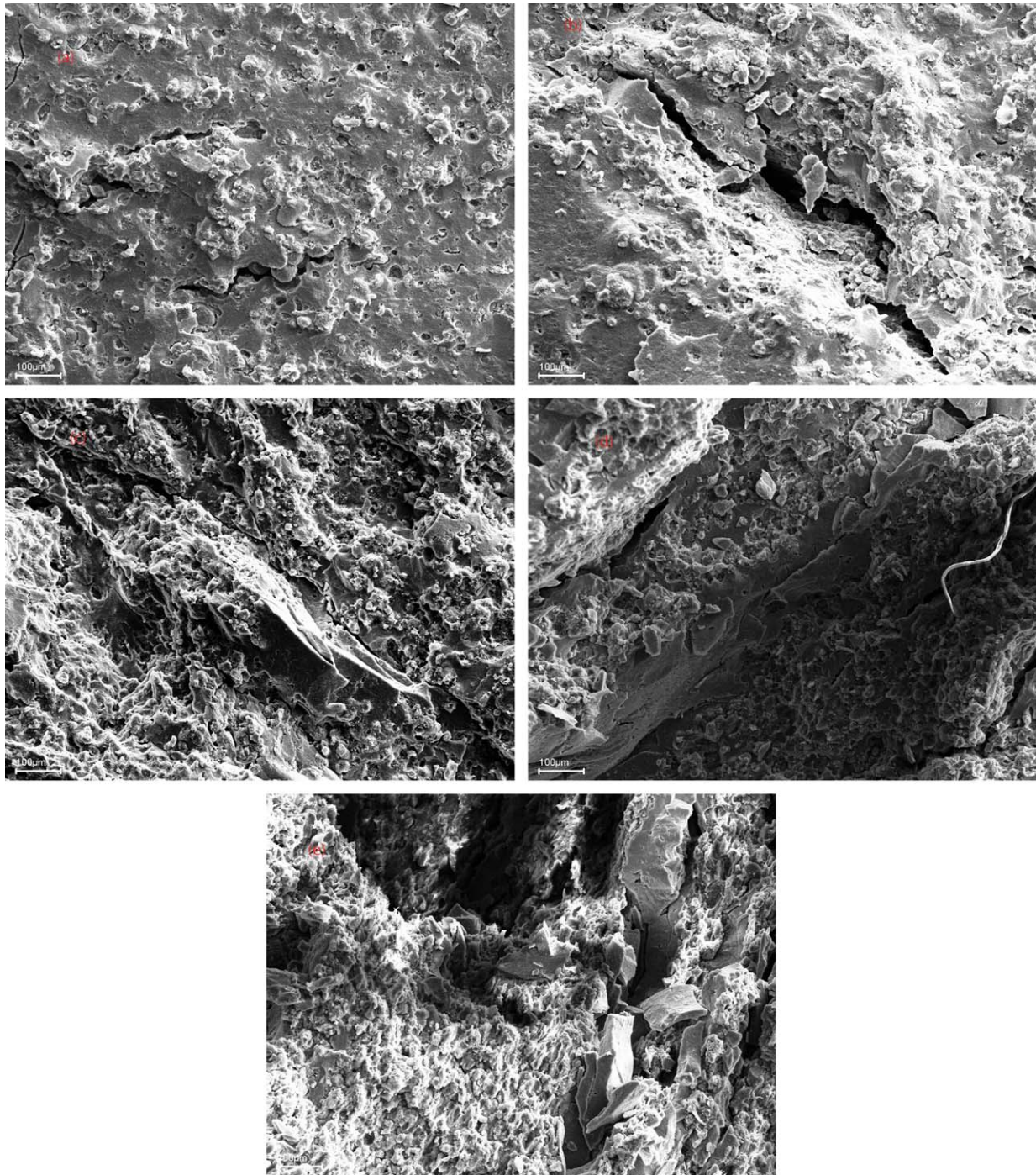


Figure 15. *Chlorella* thermoplastic blend SEM (100×). (a) 20% PE 63% CV 17% Gly, (b) 35% PE 50% CV 15% Gly, (c) 50% PE 37.5% CV 12.5% Gly, (d) 65% PE 24% CV 11% Gly, (e) 80% PE 10.5% CV 9.5% Gly.

plasticized algae blends. For *Chlorella* bioplastics, the plastic appear to become tougher as the plasticizer amount is reduced because the surface becomes more roughly textured. This means that a balance between plasticization, which increases plastic flexibility, and no plasticization, which increases stiffness is likely best reached at 80/20 or 85/15. In addition, *Chlorella* plastic appears to be tougher overall than *Spirulina* because the surface for *Chlorella* plastics are rougher.

***Spirulina* and *Chlorella* Thermoplastic Blends SEM**

Figure 14 shows SEM fracture micrographs for *Spirulina* thermoplastic blends. In general, polyethylene phases are seen in very rough areas, and smooth areas represent *Spirulina* phases. The 50% PE/37.5% SP/12.5% Gly blend formulation seems to exhibit the most homogeneous blending and least phase separation, making it the most desired formulation for good phase interaction and enhanced performance properties compared to

blends with more than 50% biomass loading. Figure 15 shows the SEMs for *Chlorella* thermoplastic blends. In *Chlorella*, blend compositions with 20% and 35% PE show little to no PE characteristics, but 50% and 80% show very little *Chlorella*-like phase properties. This may be attributed to a lack of interaction between phases, which leads to areas that are predominantly one phase in the material. In 65% PE blend, the two phases can be seen together; however, they appear to exist in adjacent planes rather than interspersed throughout the matrix. In immiscible polymer blends, the largest quantity polymer forms the continuous phase, whereas the smaller quantity polymer forms the dispersed phase.²¹ Overall, TGA, SEM, DMA, and mechanical analyses at 20%, 35%, 50%, 65%, and 80% of PE loading in *Spirulina*-based thermoplastic blends show that the 50% biomass is an optimal loading for achieving the best performance of the resulting plastic with maximum biomass loading.

CONCLUSIONS

Glycerol plasticization of microalgal biomass was determined to be most effectively accomplished at a 4:1 ratio of biomass to glycerol. Furthermore, this ratio was used to develop blends of microalgal biomass and polyethylene that demonstrated varied degrees of compatibility. *Chlorella* exhibited higher bioplastic properties, but because of a lower degree of compatibility with polyethylene it did not perform as well with polyethylene as did *Spirulina*. This incompatibility of *Chlorella* with polyethylene may result from the amino acid compositions of the two microalgae, but other factors likely play a role. Overall, *Chlorella* bioplastics performed very well even outpacing some polyethylene blends, but because the whole algal biomass does not form melts in the traditional thermoplastic sense, blending is desired for commercial usage. In blends, *Spirulina* performs much better and is therefore more desirable for commercial applications. With the addition of compatibilizers, however, *Chlorella* may benefit more significantly than *Spirulina* resulting in *Chlorella* performing better in compatibilized blends. Therefore, further study is needed to determine how compatibilizers effect the reaction of these algal bioplastics with polyolefins.

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