Sustainable Bioderived Polymeric Materials and Thermoplastic Blends Made from Floating Aquatic Macrophytes Such as "Duckweed"

Mark Ashton Zeller,[1] Ryan Hunt,[2] Suraj Sharma[1]

[1]Department of Textiles, Merchandising & Interiors, University of Georgia, Athens, Georgia
[2]ALGIX, LLC, Athens, Georgia
Correspondence to: S. Sharma (E-mail: ssharma@uga.edu)

ABSTRACT: While plastics offer many conveniences to modern consumers, they represent unsustainable practices that hinder economic growth and environmental stability. Therefore, the production of biodegradable plastic from alternative feedstocks is investigated to replace conventional plastics in packaging and short-term use markets. Duckweed represents a feedstock that elicits high biomass productivity, plus a wastewater remediation potential. To establish duckweed's potential for plastic production this study investigates the stability and thermal characteristics of plasticized and blended duckweed polymers. Duckweed biomass milled to 250 μm was plasticized using glycerol and compression molded into plastic samples. Results indicated a 3 : 1 ratio of duckweed to glycerol produced the best polymer stability. This ratio was then used to develop blends which demonstrated dispersion in biobased or polyethylene (PE) phase, except for 50% Biobased/50% PE where phase continuity was observed. Furthermore, surface morphology indicated limited homogeneity in blends and increased PE was correlated to temperature stability of biobased phase. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In our modern day, consumer society plastics have dominated the market as the premier material for most applications including packaging. This phenomenon is not completely unwarranted since conventional plastics are strong while maintaining a low weight, and offer resistance to degradation by water, chemicals, sunlight, and bacteria, as well as providing electrical and thermal insulation. All of these attributes make conventional plastics versatile for many applications; however they also come with environmental concerns. High impact polystyrene (HIPS), a commonly used plastic polymer 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 since conventional plastics are produced from crude oil, an increasingly diminishing resource, as a chemical precursor in this energy costly process that yields HIPS resin.[5] Beyond these consumption issues the process of resin production further hinders the environment by producing waste products that enter the air, water, and the ground. Some of these waste products are known toxins and other damaging compounds that can leach out over time leading to ground water reservoir contamination.[3] Further-

more, after production the same properties that make conventional plastics attractive for commercial applications also produce further environmental costs by preventing biodegradation which increases the demand and size of landfills to facilitate the increasing amounts of plastic entering the municipal solid waste stream.

One solution to these problems is recycling plastics which can reduce the filling of landfills and therefore leaching of chemicals by extending the use of a material, however, this has inherent energy consumption of its own. A study of packaging materials produced from HIPS showed that 18.9 MJ was required to produce 1 kg of recycled material, a cost that was approximately 23.5% the cost of producing the same product from raw materials.[7] So while recycling does dramatically reduce the environmental cost of producing virgin plastic materials it also has its own environmental vices. These problems make conventional plastics no longer a sustainable solution in applications like packaging and short-term use products in which large quantities of plastic materials are produced and disposed of causing significant cost to our environments.

For this purpose biobased plastics made from natural feedstocks present a biodegradable alternative to conventional plastics

significantly reducing environmental strain and the use of fossil fuel reserves. Currently, the carbohydrates fractions of biomass, such as starch and cellulose from corn, wheat, rice, and potato, have been used as base material for conversion into biobased plastics. These materials produce bioplastics such as polylactic acid (PLA), cellulose acetate (CA), and thermoplastic starch (TPS). Another approach to forming biobased polymers is to use nature's existing polymers, i.e., protein made up of amino acids. Many of these protein plastics currently studied come from terrestrial crops like soybean and sunflower seed.[10,11] Of these crops soybean has the most widely studied proteins used for making bioplastic articles and films; however, casein from milk protein also has a long history of use in making bioplastic articles and biobased paints. A primary limitation of conventional biobased plastics is that the biomass source competes with food and feed applications, similar to the arguments made against corn ethanol, as these agro-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 relatively long periods of 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 of the genus *Lemna*, more commonly known as duckweed, is an aquatic macrophyte which has a high biomass productivity, can grow on wastewater and its biomass contains large fractions of protein, starch, and fiber.[12] Duckweed has been shown to double their biomass in as little as 16 h providing large amounts of biomass during cultivation.[13] This fast growing aquatic macrophyte has protein concentrations as high as approximately 40% of its dry biomass weight under nitrogen-rich growing conditions, and can be up to 50% starch composition under nitrogen starved conditions. Duckweed also has a long history of providing bioremediation for municipal and agricultural wastewater treatment using low cost cultivation techniques.[13] Duckweed's prolific nature allows it to be harvested over short intervals for ∼ 300 days/year in warm climates like the southeastern US. Using duckweed for wastewater treatment allows wastewater, an often overlooked resource, to be remediated and reclaimed for agricultural or other on-site uses.[13] Considering all these prospective benefits combined, duckweed-based polymeric materials have the potential to revolutionize the packaging materials market into a waste free and environmentally friendly market. The objectives of this research are to determine best ratio of biomaterial to glycerin to produce optimally plasticized protein polymer; fabrication and characterization of blends of duckweed and ultra high molecular weight polyethylene (UHMW-PE), a model thermoplastic polymer used in this study.

EXPERIMENTAL

Materials

The duckweed was grown and harvested in Melbourne, FL, by VEN Consulting, LLC and was identified as a species of the genus *Lemna* and is shown in Figure 1(A). The duckweed was dried at 70°C in a forced convection dryer to a moisture con-
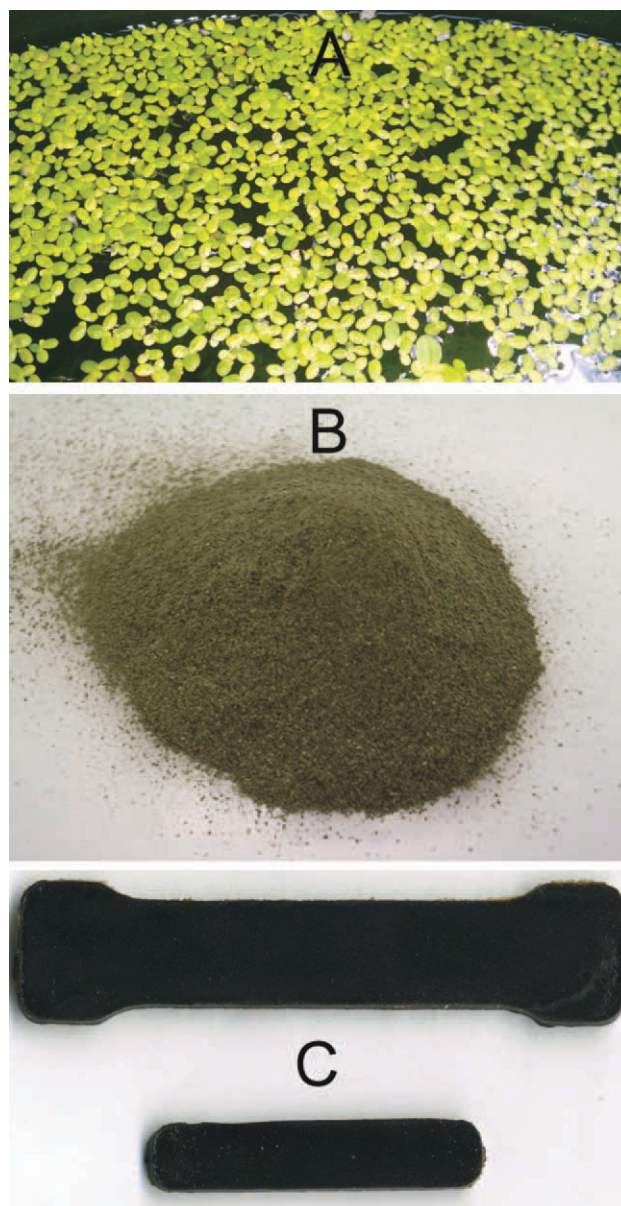
Figure 1. (A) Fresh duckweed before harvest and drying, (B) Dried and milled duckweed flour, and (C) Samples of compression molded dogbone and DMA flexbar. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tent of 11%. The samples of duckweed used in the trials were knife milled (SM2000/1690Utm, Retsch GmbH, Germany) with 0.25-mm screen and is denoted as "D.W.M." and the milled flour is shown in Figure 1(B). The milled flour was then sieved using the industrial sieving method to determine the particle distribution of its constituents. The duckweed milled material exhibited particle sizes ranging from <45 microns to >420 microns with an average particle size of approximately 200 microns. UHMW-PE powder was received from Sigma Aldrich, USA and has particle sizes of 53–75 microns with a melting temperature of 144°C. Glycerol was also obtained from Sigma Aldrich with a purity of ≥99%.

Preparation of Blended Samples

Thermomechanical molding of duckweed blends were performed on a 24-ton bench-top press (Carver Model 3850, Wabash, IN) with electrically heated and water-cooled platens. The stainless steel molds were custom made to form either a single dogbone or two small rectangular flex bars 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. Each formulation of duckweed, and glycerol were thoroughly hand mixed and then PE was added for hybrid materials followed by further mixing. The blends were made in small batches ≤5 g and then manually filled into the mold cavity to a standard weight, i.e., 1.5 g for DMA flexbars and 5.0 g for dogbones using an Ohaus Precision Standard balance. After the samples were cooled for 10 min under pressure, the pressure was released, and the samples were removed. Figure 1(C) shows samples of compression molded dogbone (top) and DMA flexbar (bottom) used.

Proximate Analysis

The proximate Analysis was performed by a LECO TGA701. The proximate analysis was conducted by a standard protocol using anaerobic proceeded by aerobic atmospheres. This test method produces data showing volatiles, ash, and fixed carbon percentages. The compositional analysis was performed using three different methods. Elemental analysis was conducted in a LECO (Model CHNS-932, LECO, St. Joseph, MI) analyzer following methods outlined in ASTMs D 5291 and D 3176. The analyzer was calibrated using sulfamethazine (C—51.78%, H—5.07%, N—20.13%, and S—11.52%) as the standard material and the crude protein content was estimated by multiplying the elemental N content by a factor of 6.25. The carbohydrate content was determined using a phenol/sulfuric acid treatment and the absorbance was measured at 490 nm on the UV–Vis spectrophotometer using a standard curve of glucose as a reference (Varian Cary 50, Varian) according to the DuBois method.[14] The lipid content was measured by gravimetric method using an ANKOM XT10 automated extraction system (ANKOM Technology, Macedon, NY) where hexane was used as extraction solvent.[15]

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed on a DMA 8000 Dynamic Mechanical Analyzer from Perkin Elmer for specimens with dimensions of $9 \times 2.5 \times 12.5$ mm 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 duplicate to ensure accuracy in measures.

Thermal Analysis

Thermal gravimetric 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 25–500°C under N_2 gas with a heating rate of 10°C/min. DSC was performed from −50 to 250°C under N_2 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 (SEM)

Samples were made from cryogenic DMA flexbar fracture surfaces. DMA flexbars were submerged in liquid nitrogen for 20 s after which they were immediately broken. All samples were prepared by mounting then sputter coating for 60 s with an Au/Pt mix. SEM images were recorded on a Zeiss 1450EP variable pressure scanning electron microscope. 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} crosshead speed with a static load cell of 1000 N and gauge length of 60 mm. The specimens were conditioned at standard conditions (20°C, 65% RH) for 24 h before testing and were run in quintuplicates. For wet tensile testing, samples were soaked in distilled deionized water for 24 h before conditioning to ensure thorough saturation.

RESULTS AND DISCUSSION

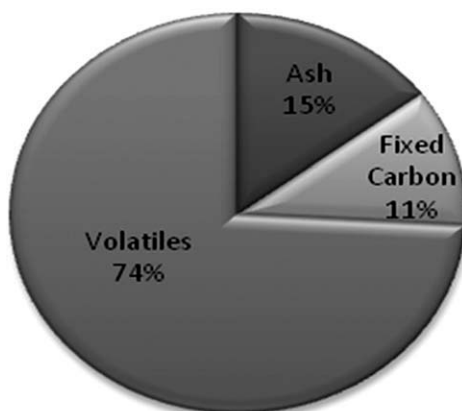### Elemental, Compositional, Proximate Analysis

The results of the compositional and elemental analysis are shown in Figure 2. It is interesting to note that crude protein content is only 19% which is low for this species and means that this harvest of duckweed may have been grown in a low nitrogen environment. This is an important consideration, because duckweed grown under higher nutrient loads, such as agricultural, municipal, and industrial effluents, may provide even better polymerization of the biomaterial matrix.

Thermal Analysis of Duckweed Biomass

TGA and DSC were performed on duckweed biomass with results shown in Figure 3. TGA results showed a three-step degradation for duckweed biomass. The first of these degradations starts at approximately 50°C and ends at 100°C. The first degradation is representative of bound water and low volatiles loss. The second degradation which begins at about 250°C and ends at about 350°C is representative of carbohydrate and protein burning since it occurs in the range where carbohydrates (e.g., hemicelluloses, cellulose, and starch) are typically degraded.[8] The last degradation is at 450°C and is very small probably the result of degradation of extremely thermal resistant materials such as lignin,[16,17] although found in small amounts in duckweed. DSC results show a strong endothermic peak at about 110°C which is demonstrating bound water loss, a peak typically seen in this range that accompanies protein denaturation.[8] This bound water can be connected to relative protein concentration due to its relation to protein denaturation. However, bound water may also accompany cellulosic or carbohydrate material so it is not necessarily directly correlated with high protein content. A second peak at approximately 180°C is also observed to a lesser extent, and this peak may represent amorphous cellulose hydrolysis which can be seen in this range.[18]

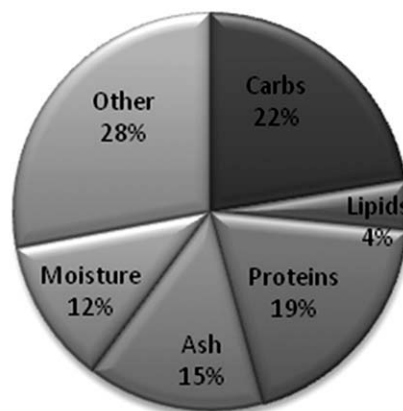## Proximate Analysis

Compositional Analysis

Figure 2. Proximate, compositional, and elemental analysis of duckweed biomass.

However, this result cannot be confirmed until further studies are done to see whether glucose is produced at this temperature range.
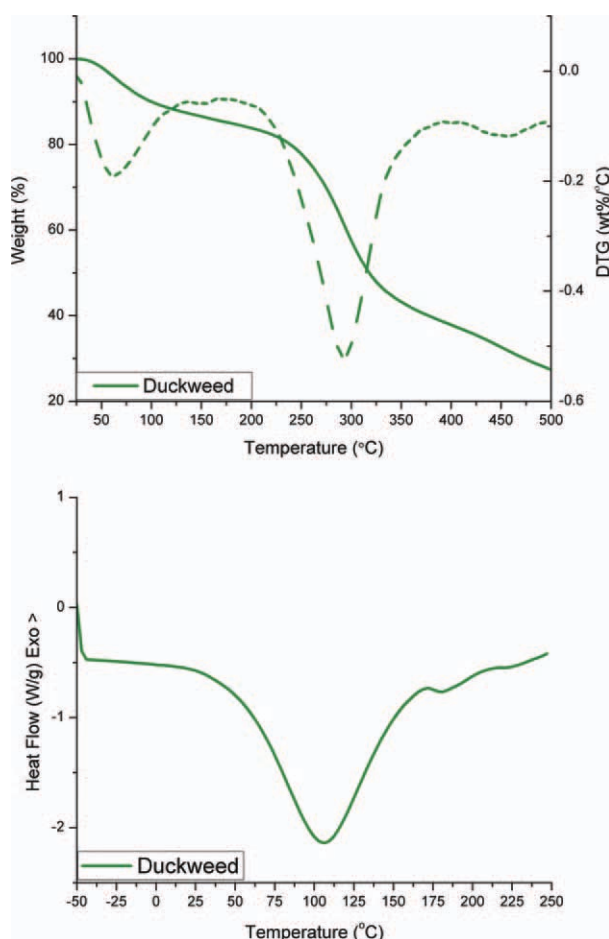

Figure 3. TGA and differential scanning analysis of duckweed raw biomass. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic Mechanical Analysis

Duckweed plastic formulations of 100% biobased and hybrids that were blended with UHMW-PE were tested on the DMA system. The DMA measurements determine the viscoelastic behavior by evaluating the elastic modulus G' (or storage modulus), which is related to the stiffness of the material, and the viscous modulus G'' (or Tan Delta), which is related to the potential for energy absorption in the sample. All DMA results shown in Figure 4 represent an averaging of duplicate DMA test runs. All of the samples aside from pure duckweed appear to have similar results, showing a substantial effect from plasticization with glycerol. The data suggest that plasticization above 25% has no additional effect since samples with 25% and 30% glycerol showed similar effects across all temperature ranges. Still, the effect of glycerol seems to be lowering modulus values and raising tan delta in conjunction with a stabilization of the material. While glycerol quantities in the middle of the loading
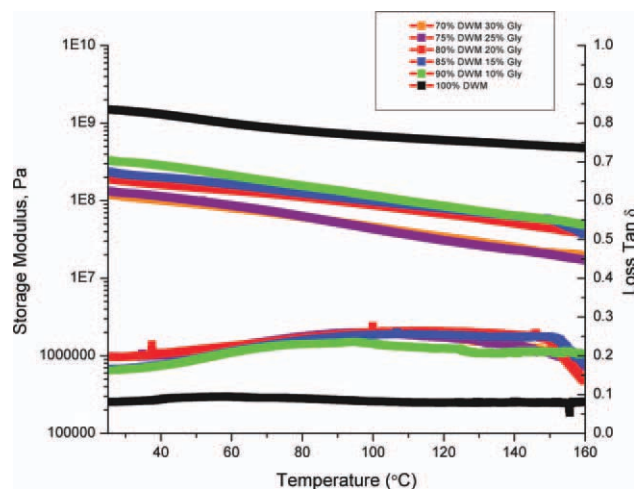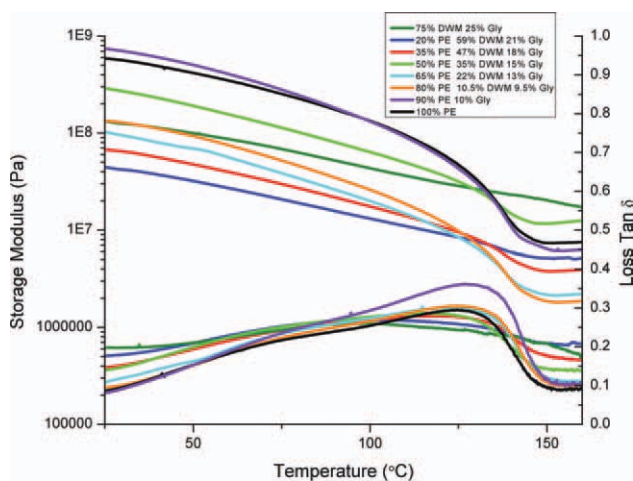

Figure 4. DMA of duckweed plasticized biopolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. DMA of duckweed blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range had maximum standard errors below 20 MPa demonstrating their relative stability, 30% glycerol had a maximum standard error of 50 MPa, 10% glycerol had a maximum standard error of 98 MPa, and 100% DWM demonstrated a standard error of 550 MPa. These standard errors highlight the lack of stability and repeatability of these samples. Since 25% glycerol was determined to be the highest ratio of glycerol achievable with good stability and higher glycerol fractions decrease the stiff and brittle characteristics of the material 75% DWM/25% glycerol was determined to be the best performing material.

Due to the observed high performance of 75% DWM/25% glycerol formulation a ratio of 1 : 3 glycerol to algae was used to calculate the glycerol quantity needed for hybrid algae/polyolefin composites. The quantity of glycerol needed to plasticize a quantity of algae in blends was determined by Eq. (1) (equation for blends plasticization)

$$\text{Quantity of glycerol} = (\text{Grams of polyethylene})(1/13.3) + (\text{Grams of duckweed})(1/3). \quad (1)$$

The equation considers the carrying capacity of PE for glycerol which was determined to be a 1/13.33 ratio of glycerol to PE (results not shown), and the ratio of glycerol to algae of 1/3 previously shown to present the maximum plasticization. Composites with 20%, 35%, 50%, 65%, and 80% PE were tested and remaining algae to glycerol percent composition was determined by use of Eq. (1). Figure 5 shows the average of two DMA results for these blends when compared with the plasticized duckweed at the 75/25 ratio, and the pure and plasticized PE resin. In general, the samples follow an expected trend for tan delta with higher PE content yielding lower initial tan deltas and larger melting point transitions, whereas higher duckweed content produces polymers that have more consistent Tan Delta values remaining almost unchanged throughout temperature range. Also Tan Delta values near the melting point of PE show 65% PE/35%

biobased, and 80% PE/20% biobased as having a greater increase than PE itself demonstrating lack of biobased phase continuity and showing that duckweed acts as a filler instead of a polymer network in these formulations. However, when observing modulus values a few peculiarities exist. Plasticized PE has the highest Tan Delta and storage modulus values till post melting and plasticized duckweed would therefore be expected to have the lowest values; however, instead only the 50% PE /50% Biobased blend has a higher modulus value than plasticized duckweed and all other formulations exhibit lower modulus values. This deviation from the linear rule of blending two polymers highlights two questions, the first being what makes the composites not fit a stiffness trend that sets them between their two components the resin and bio blend, and the second being what makes 50% PE different so that it does fit this trend? The first question can most likely be attributed to molecular interactions between the dispersed and continuous phases of blend components. Since duckweed phase consists of primarily hydrophilic interactions and PE consist of only hydrophobic interactions the matrix would be more destabilized and loosely packed due to the repulsive forces between these components resulting in weak interfacial adhesion. This reduction of polymer matrix density will have a similar effect to plasticization providing free space for polymer chains to move reducing material stiffness and modulus values. However, the reason for 50% PE /50% biobased's increased stiffness is possibly that the 50% bio based/50% PE ratio is leading to increased stability due to continuity in both algal and PE phases, while all other formulations have dispersion in one of their phases. Overall the DMA showed 50% PE/50% biobased appearing to be the best composite blend when compared with pure PE due to the stabilizing influence of this ratio.

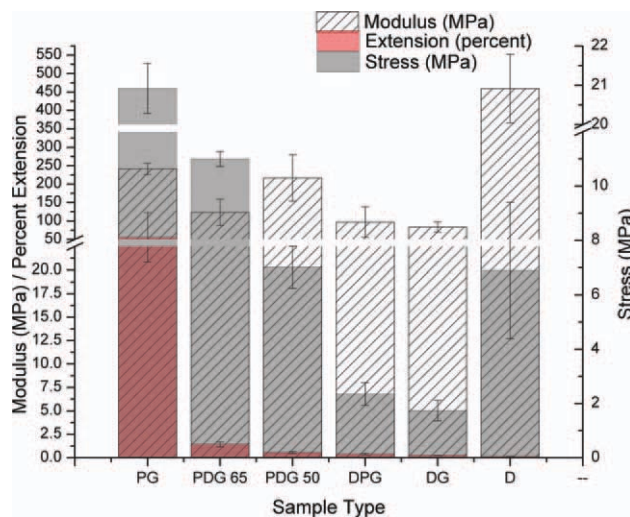### Tensile Properties of Select Duckweed Plastics

Tensile properties for select duckweed plastics are displayed in Figures 6 and 7 demonstrating percent extension and stress at maximum load, and tensile modulus data. The data collected include the top three PE/duckweed blends, the optimally plasticized duckweed material, a raw duckweed material, and a pure PE with glycerol material. The stress strain curves shown in Figure 6 display representative curves for each duckweed containing formulation type tested. In observing the stress strain curves, it is apparent that 100% DWM does not fit curve structure of an elastomeric material and behaves more like a brittle material. Furthermore, upon plasticization the duckweed material seems to behave like an elastomeric material showing similar curve dynamics to PE containing samples, but with a shorter distance from yield point to failure point indicating shorter plastic-like state transition. Similar to DMA data collected Figure 7 shows tensile modulus values for 50% PE/50% biobased are much higher than the general trend, which is theorized to be due to phase continuity in PE and biobased phase. Also in observing the results it seems to be that there is a general trend in percent elongation until 65% PE/ 35% biobased blend in which there is a significant rise in properties.

This trend which is consistent until the 65% PE/35% biobased blend demonstrates that 50% PE/50% biobased likely still has
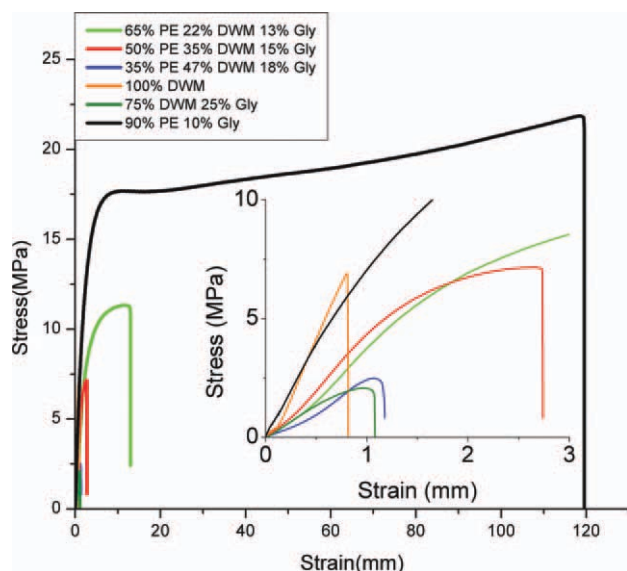
Figure 6. Stress–strain curve for duckweed containing formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

protein phase continuity. Conversely, in observing stress increase in 50% PE/ 50% biobased blend the significant increase in stress when compared with previous trend of increase indicates that 50% PE/50% biobased is different. This combination of trends therefore may indicate the dual phase continuity previously discussed and may show that protein phase is more important for determining percent elongation characteristics, and PE more dominant in determining stress characteristics. Overall as expected increasing PE content increased material properties, except in case of 50% PE/50% biobased blend's modulus which was higher (synergistic effect) than 65% PE/ 35% biobased

Figure 8. Dogbones after 24 h soaking. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blend's modulus as may have been predicted based on previous DMA results. In Figure 8 dogbones after 24 h soaking are shown with no noticeable deformation due to soaking.

In Figure 9 and Table I, the pure and plasticized duckweed samples tensile results are displayed showing substantial falls in properties for both materials. This result is expected in wet
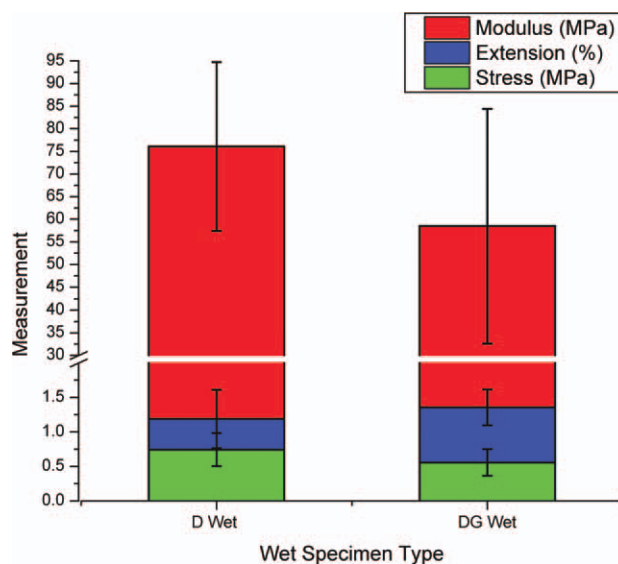

Figure 7. Tensile properties for duckweed and blends (PG = 90% PE, 10% Gly; PDG 65 = 65% PE, 22% DWM, 13% Gly; PDG 50 = 50% PE, 35% DWM, 15% Gly; DPG = 35% PE, 47% DWM, 18% Gly; DG = 75% DWM, 25% Gly; and D = 100% DWM). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Wet tensile results for biobased materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of Both Wet and Dry Duckweed Biopolymer Tensile Test with Percent Losses Shown

Comparative analysis of duckweed biopolymers before and after soaking in water				
Sample	Stress (MPa)	Extension (%)	Modulus (MPa)	Stress/Extension/Modulus Loss (%)
100% DWM	6.89 ± 2.51	2.10 ± 0.17	459.46 ± 93	89.2% (Stress)/43.3% (Extension)/83.4% (Modulus)
100% DWM Wet	0.75 ± 0.24	1.19 ± 0.42	76.12 ± 19	
75% DWM 25% Gly	1.74 ± 0.38	3.40 ± 0.28	83.63 ± 14	67.9% (Stress)/60.1% (Extension)/ 30.1% (Modulus)
75% DWM 25% Gly Wet	0.56 ± 0.19	1.36 ± 0.26	58.54 ± 26	

protein plastics since water interferes with hydrophilic interactions between protein chains, and is evidenced in prior work with soy protein films.[19] However the pure duckweed sample had much more substantial falls in material properties than the plasticized duckweed as demonstrated in Table I. This further reinforces the claim that 75% DWM 25% Gly plasticized formulation is the best for use in composite blends, since it shows an increased ability to maintain its properties after soaking. This is especially evident in modulus values, in which plasticized duckweed material showed only a 30.1% loss compared with the pure duckweed's 83.4% loss.

In Table II, duckweed polymeric materials are compared with other bioplastic examples from the literatures that have a similar formulation. From this comparison, it can be seen that whole duckweed biomass material behaves very similar to soy protein isolate and feather meal plastics in the literature. Plasticized duckweed do not exhibit the extreme increases in elongation than other bioplastics, however, they do show the same decreases in tensile strength. This lack of exponential elongation gains that is experienced by other materials but not by duckweed is likely the result of the raw nature of the duckweed material used.

While other samples in literature use purified protein or starch constituents the duckweed utilized is in its raw milled state. This likely inhibits protein polymer chains from interacting well when plasticized and therefore doesn't lead to the substantial positive elongation gains from plasticization. Since the goal of plasticization is to reduce brittleness and increase elongation at break more work needs to be done to determine if duckweed's resistance to glycerol as a plasticizer is as a result of its raw nature as theorized above or if it is due to the ineffectiveness of glycerol in this case and a more suitable plasticizer should be selected. Furthermore to better evaluate duckweed as a bioplastics material more work should be done to take duckweed from its raw state, and produce a more suitable material for polymerization such as purified protein or starch. In conclusion, while duckweed in its raw state is not as high performance as other bioplastic materials in the literature, it is shown to be at least comparable with other bioplastic materials, and with high protein raw duckweed material, or material which has been refined significant gains in material properties may be achieved.

Thermal Analysis of Plasticized Duckweed Plastic

TGA results for plasticized duckweed plastics shown in Figure 10 highlight a number of differences from raw biomass. The first degradation peak at approximately 55°C is the same water loss peak observed in raw biomass, but the second degradation seen in some samples is not observed in raw biomass. This degradation which peaks at about 210°C is representative of glycerol, because the samples with higher quantities of glycerol show more defined peaks at this point, and glycerol's flashpoint is 175°C. Glycerol degradation shows a large gap between 25% and above glycerol concentrations, and 20% and lower glycerol concentrations, which is probably due to excess glycerol being open to degradation as opposed to bound and stabilized glycerol in the matrix. The next degradation peak appears to be shifted from the raw biomass which peaks at 290°C whereas the plastic samples peak at 275-285°C and 315°C. This could possibly be due to previous denaturation of protein which leads to a loss in some carbohydrate's stability and creates a lower degradation temperature at 275–285°C. This shift of the previous peak at 290°C revealed a smaller peak at 315°C which was previously overshadowed. The last peak seen in TGA only observed in 100% DWM to a very small extent is at 450°C. The peak was observed to a similar extent in raw biomass and is probably due to the presence of lignin, but it seems to be the case that it is eliminated by plasticization with glycerol in plastics. This may be due to a stabilization that pushes this peak to higher temperatures, or it may be that this material is lost in plasticized

Table II. Mechanical Data Comparison of Duckweed to Other Common Bioplastic Materials (Materials Labeled as Plasticized Have Some Concentration Of Glycerol, and All Materials are Compression Molded Bioplastics in Either a Thick Film or Dogbone Format)

Comparative analysis of duckweed to other bioplastic materials		
Bioplastic type	Percent extension	Stress (MPa)
Plasticized wheat gluten/Starch[1]	169	1.7
Plasticized wheat gluten[2]	132.8	1.7
Zein[16,4]	8.5	25.3
Plasticized egg white albumen/Corn starch[6]	50	5
Plasticized egg white albumen/Potato starch[6]	35	4.25
Feather meal[8]	1.4	9.2
Soy protein isolate[9]	1.2	13.0
Duckweed	2.09	6.89
Plasticized Duckweed	3.40	1.74
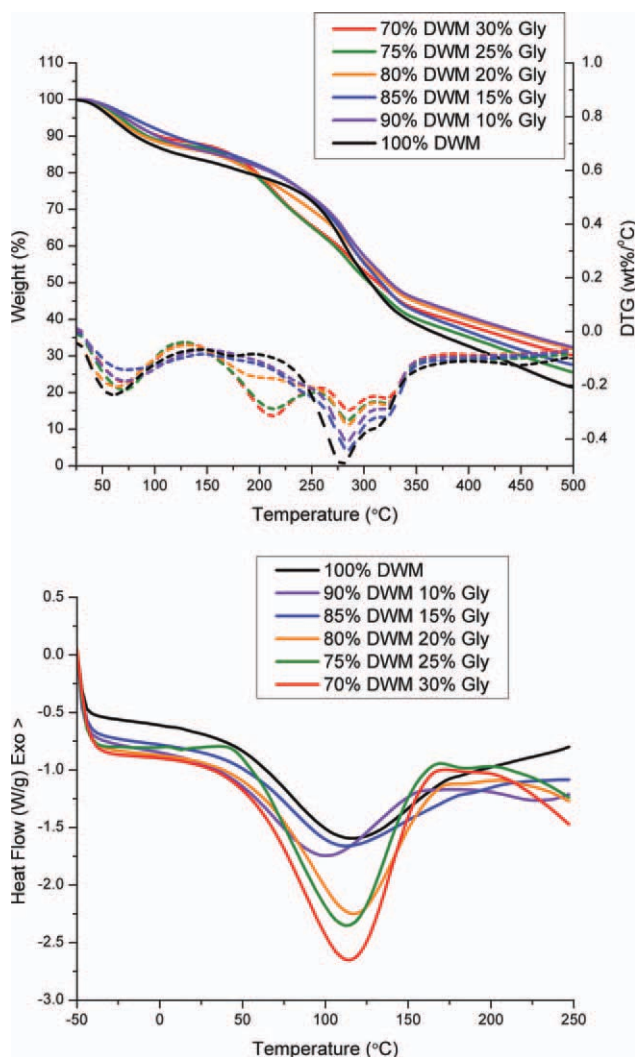
Figure 10. Duckweed plasticized plastics TGA and differential scanning analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from other sources besides protein including starch, polysaccharide, and fiber sources. Also it can be noted that increasing glycerol seems to cause more bound water to occur. This occurrence may be explained by an increase in free volume and therefore an increase in surface area over which water binding can occur. Also, it is interesting to notice the general trend of more glycerol leading to a lower temperature bound water loss which is likely due to bound water being easily evaporated out due to glycerol competition for hydrogen bonding sites. The only exception to this trend is 90% DWM/10% Glycerol which has the largest left shift. However, the stability and repeatability of this formulation has already been pointed out as questionable, so it is possible that this sample is not very homogenous and contains low matrix stability at the point sampled leading to early bound water loss.

Duckweed Blends Thermal Analysis

TGA results for blends shown in Figure 11 highlight a significant stabilization of duckweed when blended with UHMWPE. Water absorption is dramatically reduced since the water

Figure 11. Duckweed blends: TGA and DSC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
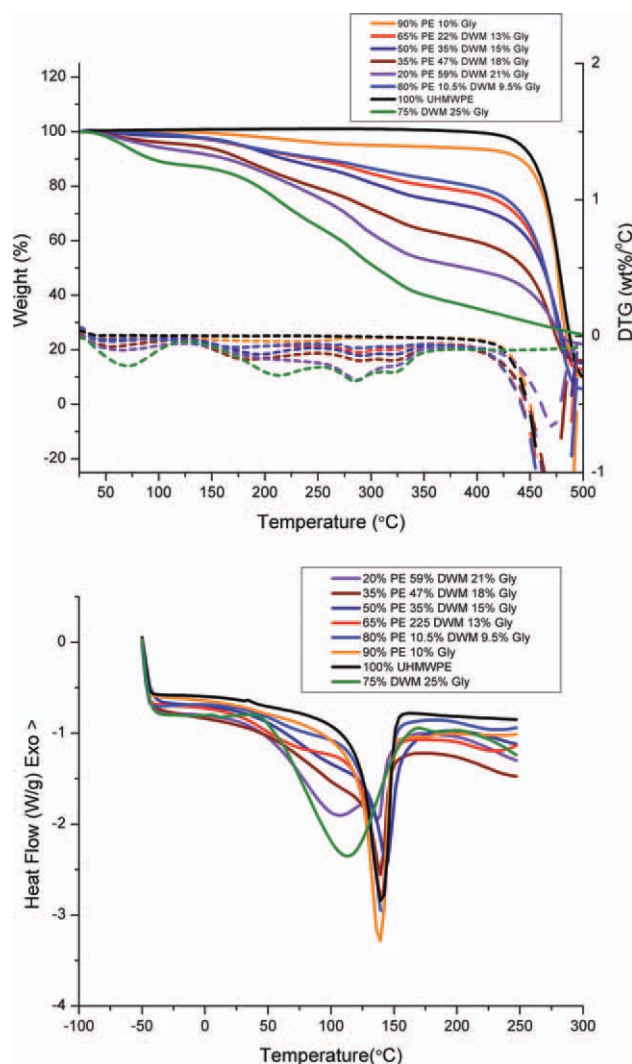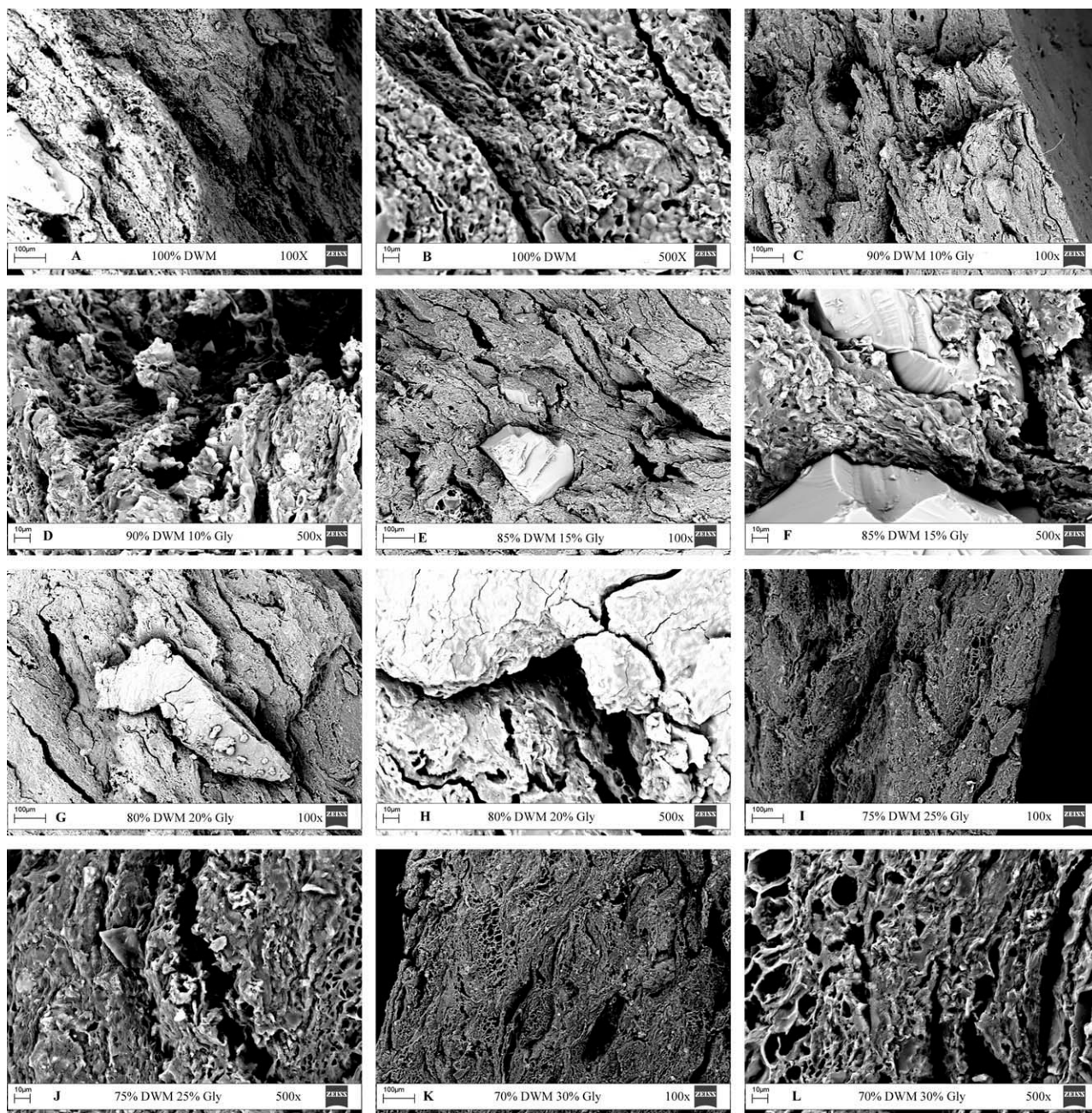
duckweed polymer production. Most of the derivative peaks follow a general trend of less degradation with increased glycerol except for the glycerol and water degradation peaks. For the glycerol peak, unused glycerol is responsible for higher degradation loss; however, the water peak doesn't have a noticeable trend, but 85% DWM/15% glycerol formulation showed smaller degradation than other formulations. This may be a random occurrence; however, it requires further study since water resistance is a major problem with protein polymers. So if this is actually a consequence of formulation then it would be interesting to determine why this formula shows this improvement.

DSC results for plasticized duckweed polymers also shown in Figure 10 display the same peak characteristic of raw biomass at between 100 and 125°C depending on sample. This peak as described earlier is representative of bound water loss which is related to protein denaturation. It is interesting that this peak is so substantial since in plastics protein should be completely denatured meaning that a large quantity of bound water comes

Figure 12. Scanning electron microscopy of plasticized duckweed fracture surfaces.

degradation peak at about 75°C is significantly lower. This is probably due to the hydrophobic nature of PE which limits water's access to duckweed material in matrix. Furthermore glycerol degradation is virtually eliminated as well with increasing PE content which may be the result of PE promoting protein denaturation leading to more interaction with glycerol. PE would promote protein denaturation by providing faster heating across the sample by increasing thermal diffusivity of matrix. The thermal diffusivity values in the matrix consist of glycerol (0.09 mm^2/s), water (0.14 mm^2/s), biomass (closest relative in the literature is low density softwood 0.17 mm^2/s), and PE (0.2 mm^2/s) meaning that PE increases the thermal diffusivity

of material and thereby increases heat transfer across material.[20–22] This increased heat transfer would lead to more protein denaturation and more glycerol utilization which would stabilize glycerol resulting in the significant drop in degradation in glycerol range. The next two peaks both show incremental reduction in degradation that correspond to biomass constituting smaller and smaller quantities of the formulation, except in the case of the carbohydrate degradation at 285°C with 20% PE/80% biobased sample. However, this is most probably due to a decrease in homogeneity that increased the presence of the material degraded at this temperature. The last of the peaks in duckweed plastics at 450°C is potentially still present in blends;
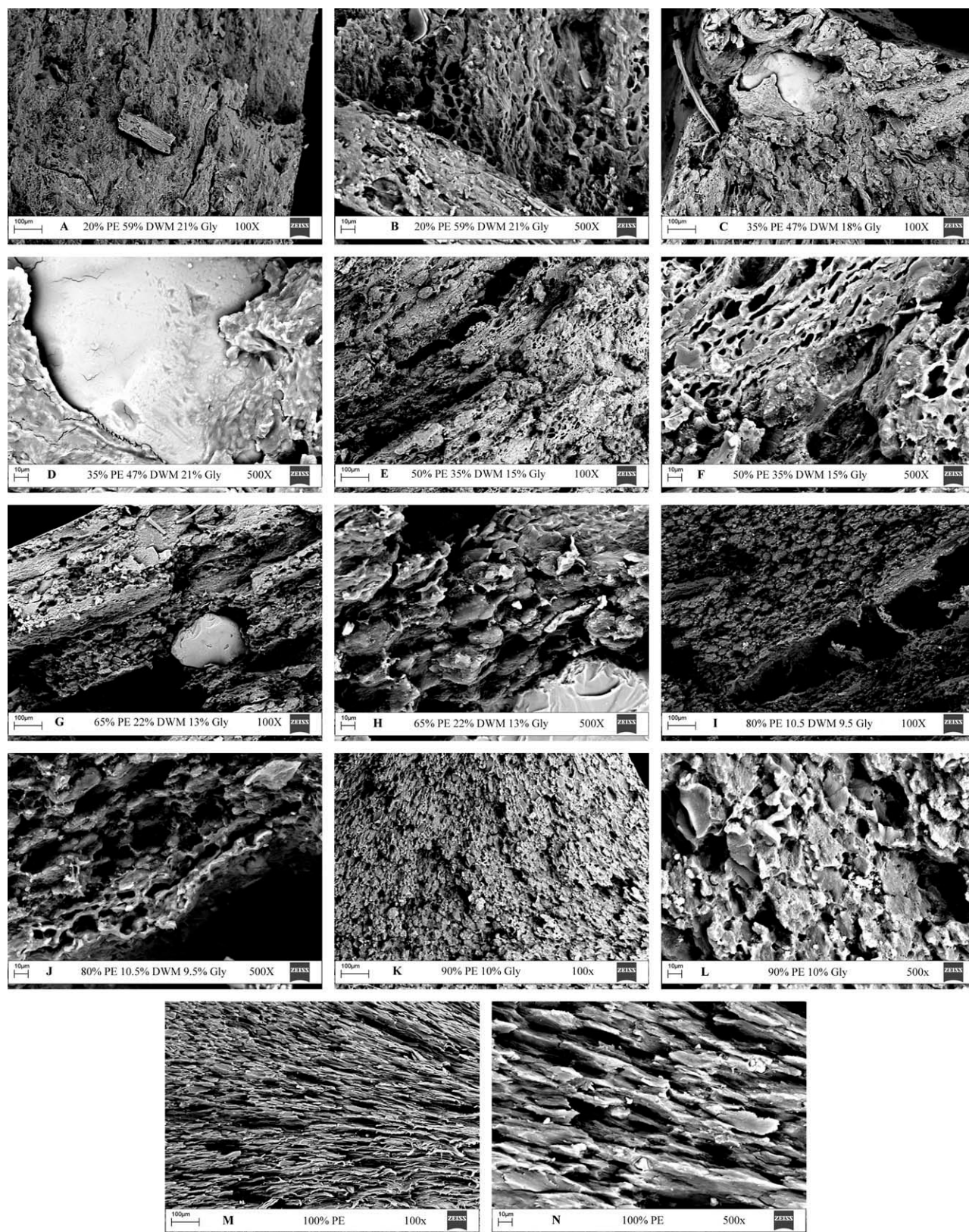
Figure 13. Scanning electron microscopy of duckweed blend fracture surfaces.

however, PE begins to degrade at this point making this peak hidden under the large PE degradation peak. Overall, it appears that blending DWM with PE even in smaller quantities can significantly increase temperature stability up until PE degradation at 475°C after which they degrade very fast.

DSC results for blends shown in Figure 11 give important temperature stability info regarding duckweed blends produced. Bound water in samples is confirmed to be largely eliminated as the PE ratio increased because the peak at around 120°C is seen to significantly decrease. Furthermore, melting of the PE phase is seen to start at about 120°C and peak at about 138°C which means that these blends would not be good for use above approximately 115°C to prevent risk of melting. Overall blends are shown to possess much better water stability than protein plastic counterparts, as well as possessing significant thermal stabilization effects.

Scanning Electron Microscopy of Plasticized Duckweed Plastics

SEM images of plasticized duckweed plastics shown in Figure 12 give morphological representations of improvement due to plasticization. The 100× magnified images seen in A, C, E, G, I, and K show how plasticization affects material phase continuity. In 100% DWM shown in image A, the break is very rigid and there are easily distinguishable, heterogeneous phase due to protein aggregation showing that material did not properly denature and form a matrix.[23] This same characteristic holds true, though to a lesser extent in image C which represents 90% DWM 10% Glycerol; however, in images E, G, I, K the protein aggregation and phase separation become less apparent where an increase in glycerol seemed to produce less heterogeneity. In fact by image I it seems to be the case that the matrix is continuous with only occasional porous zones playing a role in distinguishing which areas may be of different composition. The porous zones exist in all materials and likely represent vascular tissue in the original duckweed material biomass; however, aside from these pores the matrix seems to be very consistent. Looking at 500× magnification images (B, D, F, H, J, and L), it seems to be the case that 100% DWM has the stiffest break with 80% DWM 20% Glycerol having the cleanest break, indicating potentially tougher material without plasticization, however, surface texture is highly area specific and the differences in roughness of breaks are not different enough to say that any material is definitely tougher than another. Also in images A, E, and F impurities are noticeable that are the result of using wild grown biomass as opposed to biomass grown in a controlled environment.

Scanning Electron Microscope Images of Duckweed Blends

SEM images for duckweed blends shown in Figure 13 demonstrate morphology changes in different duckweed blends. 100× magnification images (A, C, E, G, I, K, and M) show a progression from 20% PE/80% biobased composite being smoothest break to 100% PE and 90% PE/10% Glycerol being roughest breaks. In general, immiscible blends with different blend ratios exhibit dispersed/matrix type of morphology.[23] In addition, the presence of cracks and faults indicate weak interfacial adhesion between two phases. The 20/80% PE/biobased and 80/20% PE/

biobased composites illustrated very little evidence of two distinct phases and therefore do represent the disperse/matrix morphology of a blend very well.65/35% PE/biobased composite is more representative of a homogenous blend; however, it still is very easy to recognize the difference between PE and duckweed biomass phases showing that it is not a well blended formulation. Both 35/65% PE/biobased and 50/50% PE/biobased composites showed no noticeable difference between phases indicating well-mixed blend. When observing samples at 500× magnifications (B, D, F, H, J, L, and N), the roughness of cryogenic fractures can be compared to determine matrix strengths. The 100 PE, 90/10% PE/glycerol, and 80/20% PE/biobased composites seemed to possess high toughness due to rough, undulating surface features. The 100% appears to be the toughest but all three are similar, and the 65/35% PE /biobased composite has a similar phase but also includes a more smooth break area that is characteristic of plasticized duckweed plastics. The 20% PE/80% Biobased composite appears very similar to 75% DWM/25% Glycerol with a very pourous surfaces and some roughness, and 35% PE/65% Biobased composite has a large impurity, but overall appears to have relatively smooth finish indicating low toughness. 50% PE/50% Biobased composite is like 75% DWM 25% Glycerol in architechture being very porous and relatively smooth, however, it seems as if PE coats this structure since PE like structures are seen on and around pourous structures, sometimes even occupying porous material free space. Furthermore, 100% PE, 90% PE/10% Glycerol, and 80% PE/20% Biobased composite show orientation of surface morphology indicating direction of stress demonstrating matrix toughness and resistance to stress. However, all other blends show no obvious orientation in morphology that would indicate toughness, whereas they all demonstrated more random breakage patterns that do not exhibit proper stress distribution throughout matrix. From these results, it is clear that the toughest material is pure UHMWPE, but the 50% PE/50% biobased composite ratio seems to have the best composite properties utilizing the duckweed arcitechture and then building on it to produce a sturdy material as also evident from DMA analysis.

CONCLUSIONS

Glycerol plasticization of raw duckweed biomass was determined to be most effectively accomplished at a 3 : 1 ratio of biomass to glycerol. Furthermore, this ratio was used to develop blends of duckweed biomass and PE that demonstrated good stability and matrix characteristics. Of these blends, a 50% PE/ 50% Biobased blend was capable of replacing 50% of material by weight while also, utilizing a continuous phase stabilization effect to significantly enhance modulus values and set it apart from other composites. However, in general, as PE concentrations increase material tensile strength and elongation increase so that any blend with 35% PE or more by weight was considered to be worth investigating their potential in future molding trials. In the future studies, this effect may be further enhanced by the addition of compatibilizers that will encourage interaction between phases, and create a unified matrix with enhanced toughness characteristics. Furthermore, in wet tensile testing duckweed polymeric materials held their shape, and had

property losses reduced by application of glycerol for plasticization. These results demonstrate how plasticization increased plastic-like properties in protein rich materials and yielded more stable and durable materials. Overall, a method was demonstrated for the production of stable blends utilizing raw duckweed biomass, and further studies will be done to further enhance this technology, and to determine effectiveness using common industrial plastic production practices.

ACKNOWLEDGMENTS

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