Filamentous Green Algae Additions to Isocyanate Based Foams

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ABSTRACT: Filamentous green algae, *Cladophora glomerata,* obtained from rivers and streams in California was used as a filler in isocyanate-based foams. Up to 40 wt % dried and chopped algal fibers were added to the isocyanate–polyol mix. The algal fibers and foam samples were examined by scanning electron microscopy. The effective hydroxyl number of the algae and the tensile and compressive properties of the composite foam were measured. The results indicate that foams with a uniform cell size were obtained for algal fiber lengths between 500 and 600 μm. Peak mechanical properties were obtained for algae concentrations between 5 and 10 wt %. The elastic modulus of the foam follows a power law relationship with density, with an exponent of 1.6. The overall hydroxyl number for the algae is around 300. The hydroxyl groups in the algae can serve as efficient sites for reactions with isocyanate and hence algae fibers can act as reinforcing fillers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2469–2477, 2004

Key words: algae; polyurethane; isocyanate; polymer; composite

INTRODUCTION

The properties of isocyanate-based foams such as polyurethanes can be modified by the addition of fillers.[1–5] Fillers can be used to improve modulus, impact strength, and thermal resistance; to control the color; to improve biodegradability; and to decrease the cost of the product.[6] Both inorganic (e.g., glass, $CaCO_3$, talc, mica) and organic (e.g., wood flour, jute, flax, etc.) fillers were added to isocyanate-based foams. It was shown that cellulosics such as wood flour are inexpensive, readily available, and compatible with polyurethanes.[7] The reaction of isocyanate with active hydroxyl groups may also act to covalently bond the polyurethane matrix and the cellulosic filler.[8] Cellulose is the main component in many plant cell walls. One of the common occurrences of cellulose is in a number of species of algae.[9–11] In the case of *Cladophora glomerata*, the cellulose content may be as high as 45% of the dry weight, with almost 50% crystallinity.[12] The cellulose content in the cell walls of these species is on the same order of magnitude as wood.[13] The filamentous green algae grow mainly in fresh waters.[14] The individual cells are separated by the development of a cross wall composed of the same cellulose chains. Individual fibers may branch, develop from an attachment to a substrate, and grow while floating freely if broken free from the basal cells.[15,16] *Cl. glomerata* has been found in many parts of the world including North America, Europe, and Japan.[17,18] This availability has encouraged a number of biological investigations of the algal structure and the potential application of these materials with thermoplastic matrices for the development of biocomposites.[19–22] The purpose of this investigation was to examine the use of dried algal fibers as fillers in isocyanate-based foams. The addition of algal fibers to synthetic polymers may enhance cost effectiveness and the biodegradability of isocyanate-based foams. A procedure was developed to incorporate the algal fibers in the foam. The influence of algae concentration on the mechanical properties of the foam was studied.

EXPERIMENTAL

The algae was collected from rivers and streams in California. The fibers were dried in the sun at the point of collection and ground in a Waring laboratory blender to obtain fibers of different lengths. The blending time was varied to obtain the chopped fibers of the desired length. The average length of the fibers was measured by scanning electron microscopy and fibers with an average length of $\sim$ 600 μm were used in most experiments. To determine the accessibility of the functional groups in the algae during the isocyanate–polyol reaction, the hydroxyl number (OH#) for the algae was measured according to ASTM D4274-88.[21] The OH# was calculated by reacting the algae with acetic anhydride in pyridine, followed by titration with NaOH.

The isocyanate-based foams were produced by reacting the two main components, polyol and isocyanate, and various other additives to control the structure of the foam.[21] The polyol, supplied by Miles Inc. (Pittsburgh, PA), consisted of a mixture of 55.5% Multranol 9157 and 45.5% Multranol 9171. Multranol 9157 is a propylene oxide based triol with the following structure:

$$CH_2—(O(CH)_2—C(CH)_3H—O)_xH$$
$$|$$
$$CH—(O(CH)_2—C(CH)_3H—O)_yH$$
$$|$$
$$CH_2—(O(CH)_2—C(CH)_3H—O)_zH$$
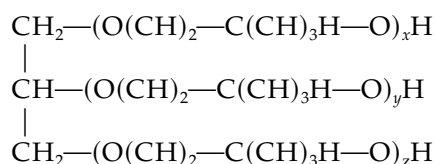
where $x + y + z = 10$, resulting in an average molecular weight of 675 and a hydroxyl number between 240 and 260. Multranol 9171 is a sucrose-based polyether polyol with a molecular weight of 1060, a functionality of 6.4, and a hydroxyl number between 330 and 350. The functionality of this polyol mixture was 4.5 and the hydroxyl number was 290. The isocyanate, Mondur MR light, with $NC_{equivalent}$ of 425, was also supplied by Miles Inc. It consisted of 4,4'-diphenylmethane diisocyanate and higher oligomers, with a $NC_{equivalent}$ of 425 and the following structure:

OCN—⟨benzene ring⟩—H_2C—⟨benzene ring⟩—NCO
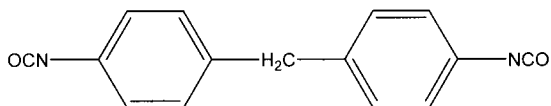
Two main additives were used to control the foam structure. They included *n*-pentane (Alfa Aesar, Wardhill, MA) as the blowing agent (typically 5–10%) and a surfactant (L6900) supplied by Union Carbide (Danbury, CT). Foams were obtained in small batches through hand mixing. Initially, all components except the catalyst were stirred together at room temperature to achieve uniform dispersion. The chopped algae fibers were directly added to this mixture. Experiments were conducted with the algae weight fraction in the foam ranging from 0 to 40%. The catalyst was then added and the mixture was blended at 7000 rpm for 10 s. In most experiments, triethylene diamine in dipropylene glycol (TEDA), supplied by Union Carbide, was used as the catalyst. Typical cream, rise, and tack free times were 15, 60, and 150 s, respectively. The blended mixture was poured into aluminum molds at room temperature, to produce cylindrical rods (65 mm diameter and 100 mm long) or tensile samples (Fig. 1) according to ASTM D1623. The foams were examined by optical and scanning electron microscopy to characterize the cell structure in the foam and to determine the distribution of the algal fibers. Specimens with a height of 30 mm and diameter of 65 mm were obtained from the central portions of the cylindrical
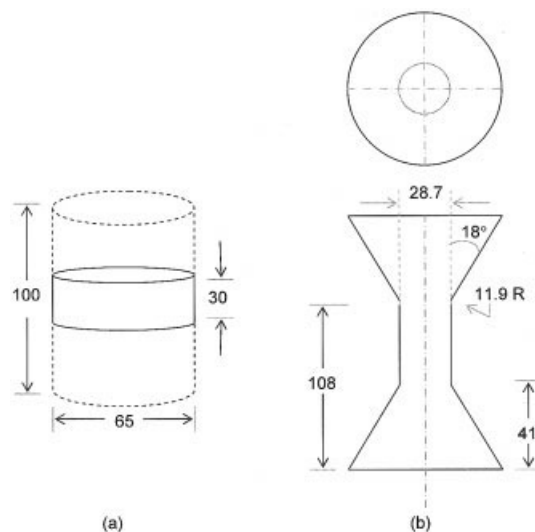

Figure 1 Schematic of the test patterns used to measure the compressive (a) and tensile (b) properties of the foam. The specimen for the compression test was obtained from the central portions of the molded part as shown in (a). All dimensions in mm.

blocks and were used to test the compressive properties of the foam (Fig. 1). The samples were cured for at least 48 h before mechanical testing. The tensile, compressive, and ball rebound testing of foam samples were conducted according to ASTM standards D1621, D1623, and D3574, respectively. Most tests were conducted at a strain rate of 1.3 mm/min. An extensometer was used in most specimens to measure the displacement. A minimum of five measurements were conducted under each condition.

RESULTS AND DISCUSSION

Two types of filamentous green algae were collected initially: *Cl. glomerata* (cotton mat algae) and the coarser horsehair algae *Pithophora oedegonia*, as shown in Figure 2.[21] Because *Cl. glomerata* is more readily available than *P. oedegonia*, it was used in most experiments. The typical structure in *Cl. glomerata* is shown in Figure 3. In general, the filaments contain numerous cylindrical cells, which are attached in series to form the fiber. The cells range from 20 to 200 μm in diameter, with length-to-breadth ratio between 1 and 25.[24] Individual plants may grow to over 1 m in length. Each filament may contain the structural cell wall (A), cross wall (B), and internal cell material (C), as shown in Figure 4. The habitat of most aquatic plants does not require strong cell walls, but in the case of *Cl. glomerata*, drag from water flow may necessitate the incorporation of structural cellulose in the cell wall. The cell wall contains large amounts of cellulose arranged in microscopic bundles called microfibrils.[21] The arrangement of the microfibrils in the fiber is

(a)
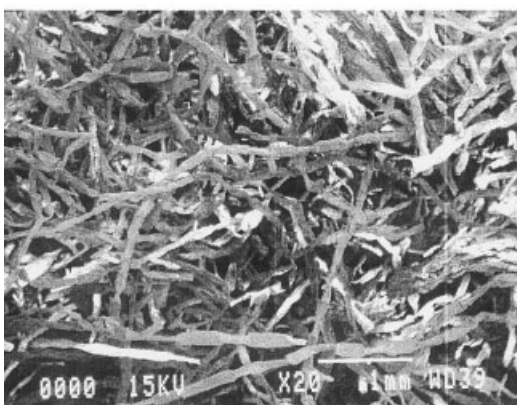
(b)

Figure 2 Photographs showing the structure of filamentous green algae after water collection from rivers and streams in California. The algal fibers were dried in the sun at the point of collection. (a) *Pithophora oedegonia*. (b) *Cladophora glomerata*.

determined by the environmental conditions during growth. The filaments are branched pseudo-dichotomously, as seen in Figure 3(A, B). Branching may
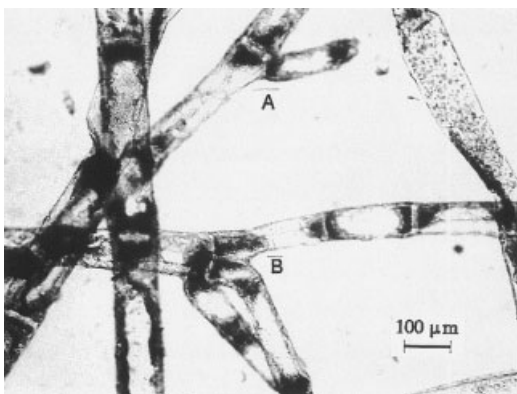

Figure 3 Photograph showing the structure of *Cladophora glomerata* filamentous green algae. Pseudo-dichotomous branching is shown at locations (A) and (B).
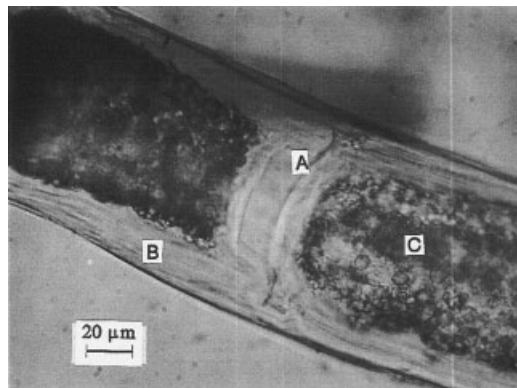

Figure 4 High-mbgnification photograph of the cellular structure in *Cladophora glomerata* showing the cell wall (B), cross wall (A), and internal cellular material (C).

occur at almost every cell or may occur infrequently, depending on growth conditions. *Cl. glomerata* grows in many natural environments and it follows that there are interactions between the algae and its ecological surroundings. As a result, many foreign species, known as symbions, may attach onto the surface of the growing filament (Fig. 5). Symbions use the *Cl. glomerata* as a substrate. The presence of the symbions on the cell walls may affect the surface characteristics of the algae.

The tensile modulus and strength of *Cl. glomerata* were measured to be on the order of 1–5 GPa and 20–45 MPa for dried fibers.[24] Typical breaking strains are between 1 and 3%. The tensile properties can vary depending on the time of the season at which the algae is harvested. Samples harvested in early season (spring) may not have fully developed cell walls and, therefore, may exhibit relatively low strength compared to algae collected in peak season (summer). The hydroxyl number for the algae was estimated to be on the order of 300.
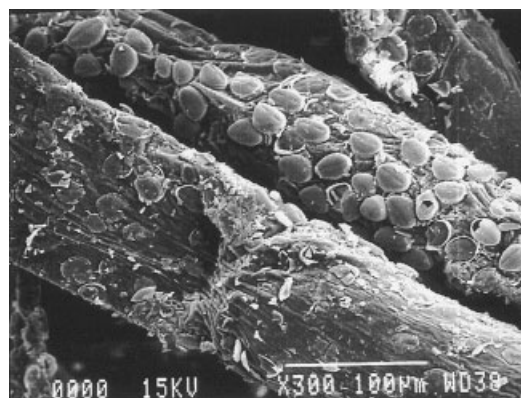

Figure 5 Photgraph showing the structure of *Cladophora glomerata* filaments with the symbionic diatoms at the surface.
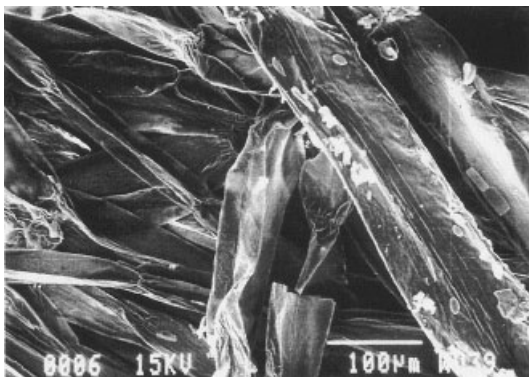
Figure 6 Photograph showing the collapse of cell body and flattening of some algal filaments after drying of the wet *Cladophora glomerata* algae.

The drying of the algal filaments may lead to collapse of the cell body and flattening of some algal filaments (compare the structure of algae in Figs. 5 and 6). It was observed that a greater fraction of the filaments exhibit collapse after drying in *P. oedegonia* algae than in *Cl. glomerata* algae (Fig. 7). The morphology of the dried filaments enables the implementation of simple grinding techniques to form short fibers. The initial structure in the dried algae was almost like a porous mat with long, interconnected fibers. Grinding may lead to separation and chopping of the fibers. For short grinding times (<20 s), the short fibers are broken down, while the long fibers may still be intact. Further, the individual fibers are not thoroughly separated. The fibers begin to break down and separate for grinding times > 60 s. At large grinding times (>150 s), the fibers are almost reduced to a powder. The average size of the chopped fiber was between 750-1000 and 500–700 μm for grinding times of 20 and 60 s, respectively. In addition, the grinding of the algae may also remove some of the symbions that are attached on the surface of the algae.
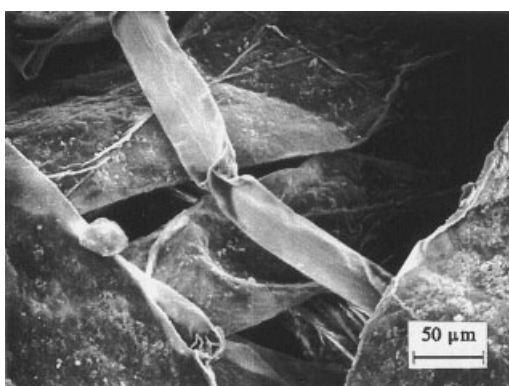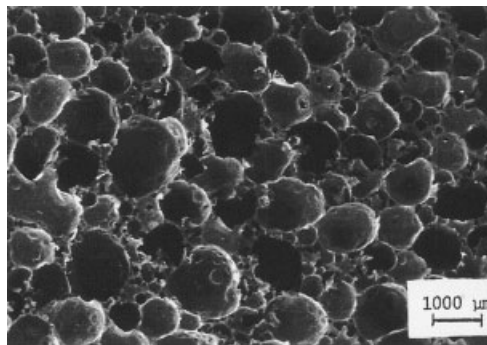

Figure 8 Photograph showing the structure in the polyurethane foam with about 10 wt % algae. The algal filaments were dried and ground to obtain an average fiber length of about 600 μm.

The foams consist predominantly of a closed cell structure with pore diameters on the order of 500-1000 μm (Fig. 8). A dense surface skin was also present on all the molded samples. The thickness of this skin was typically on the order of 3–5 mm. The length of the fiber after grinding had a significant effect on the morphology of the foams. As the average fiber size decreases, the effective number of nucleation sites may increase, leading to a small cell size in the foam. If the fiber size is reduced substantially (i.e., by overgrinding), then the algae particles may agglomerate and cause improper penetration of the isocyanate–polyol mixture between the algae. Under these conditions, foams with poor characteristics may be obtained (Fig. 9). Optimum foaming as shown in Figure 8 was obtained with algae fibers with an average size between 500 and 700 μm (i.e., grinding time of 60 s). The amount of algae added to the isocyanate–polyol mix had a significant effect on the foam characteristics, as shown in Figure 10. As the amount of algae increases, the viscosity of the suspension increases, thereby af-

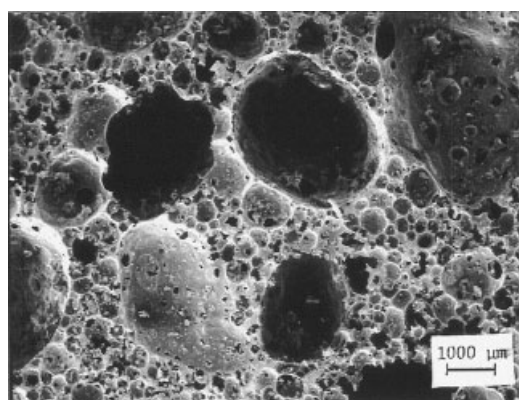**Figure 7** Photograph showing the structure in *P. oedegonia* species of filamentous green alga.

Figure 9 Photograph showing the structure in the polyurethane foam with about 10 wt % algae. The algal filaments were dried and ground to obtain an average fiber length of about 800 μm.
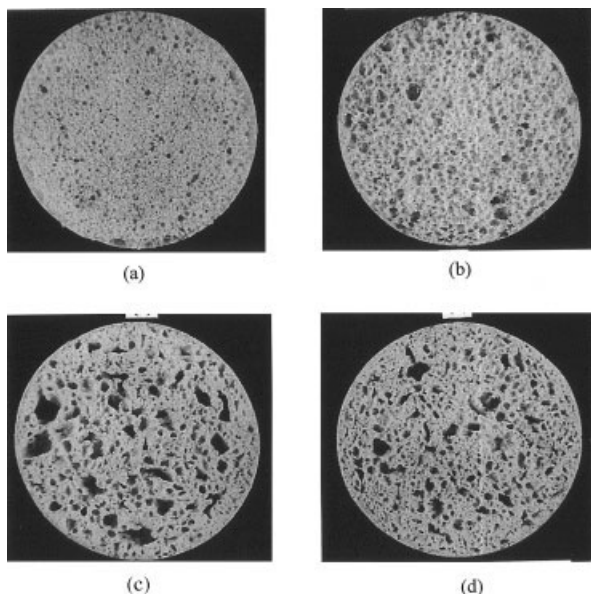
Figure 10 Photographs showing the structure of the polyurethane foam for various amounts (wt %) of algae: (a) 2.5, (b) 6.5, (c) 13, (d) 20. In each case, the algal filaments were dried and ground to obtain an average fiber length of about 600 μm.
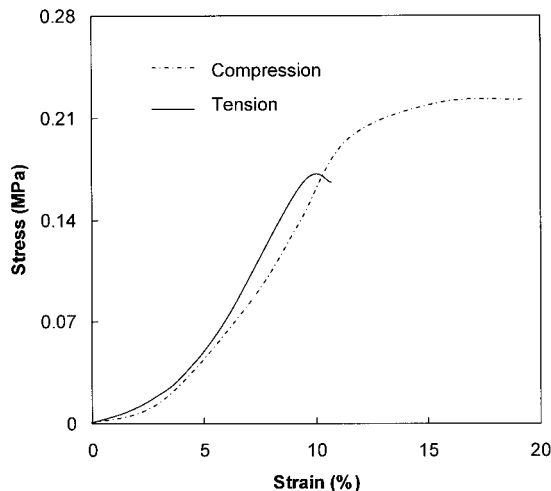

Figure 11 Typical stress–strain curves in tension and compression for the polyurethane foams with *Cladophora glomerata* algae. Both tests were conducted at a strain rate of 1.3 mm/min.

fecting the free-rise of the foam. A more uniform pore structure is observed in the foam for algae concentrations less than about 10 wt %. At high concentrations of algae, the pore structure becomes inconsistent with some large pores mixed in with average sized pores [Fig. 10(c)]. This behavior may be related to the agglomeration of algae fibers at high concentrations. The agglomeration may lead incomplete penetration of the polymerizing liquids. The pore stability may be reduced with the addition of a large number of filler particles and the gas bubbles may coalesce at the agglomeration site to create an uneven pore structure.

Typical stress–strain curves in the foam are shown in Figure 11 for tensile and compressive loads. The mechanical behavior during the initial stages of tension and compression are similar. This behavior suggests that the microstructural phenomena governing the elastic deformation under tension and compression are similar.[25] In compression, the specimens show abrupt yielding and a sustained plateau resulting from the elastic collapse and cell wall buckling of the foam.[26]

The elastic modulus from tension and compression data is plotted in Figure 12 as a function of foam density. In general, the modulus data obtained from tension and compression are similar. The elastic modulus of the foam, E^*, appears to follow a power law relationship with density, ρ^*, [$E^* \propto ([\rho^*]^n$]. Best fits were obtained with the power law exponent, n, of about 1.6. Similar data were reported by Goods et al.[27] for a closed cell polyurethane foam. Gibson and

Ashby[26] have developed the following equation to relate the elastic modulus of the foam with its density for closed cell foams:

$$\frac{E^*}{E_s} \approx \phi^2\left(\frac{\rho^*}{\rho_s}\right)^2 + (1 - \phi)\left(\frac{\rho^*}{\rho_s}\right) \qquad (1)$$

where E^* and E_s are the elastic moduli of the foam and the solid polymer and ρ^* and ρ_s are the corresponding densities. In closed cell foams, the polymer can reside in the cell struts and cell faces (or walls). The fraction of the polymer contained in the cell struts is defined as ϕ in eq. (1). At relatively high densities, the first term
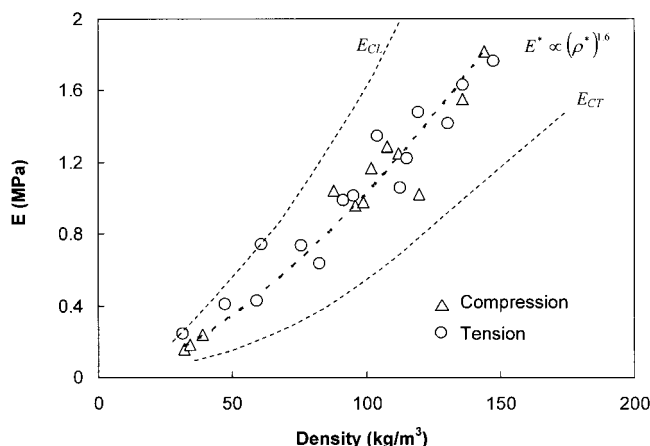

Figure 12 Variation of tensile and compressive elastic modulus with foam density. The data were fitted to a Power law equation. Best fits were obtained with an exponent of 1.6. The longitudinal (E_{CL}) and transverse (E_{CT}) modulus of the composite foam calculated from the Halpin–Tsai model are also shown. (Weight fraction of algae = 10%.)

in eq. (1) dominates and, hence, elastic modulus varies as the square of density. On the other hand, at low densities, the second term in equation becomes significant, and the dependence of E^* on ρ^* may become more linear. The observed fit with the present data (i.e., Power law equation with an exponent of 1.6) is clearly between the two extremes described above.

The Halpin–Tsai model can be used to predict the mechanical properties in fibrous composites.[28] The longitudinal modulus, E_{CL}, and the transverse modulus, E_{CT}, of the composite can be calculated by

$$E_{CL} = E_P\left(\frac{1 + \xi\eta V_a}{1 - \eta V_a}\right) \qquad (2)$$

$$E_{CT} = E_P\left(\frac{1 + \eta V_a}{1 - \eta V_a}\right) \qquad (3)$$

where

$$\eta = \frac{\dfrac{E_a}{E_P} - 1}{\dfrac{E_a}{E_P} + \xi} \qquad (4)$$

and

$$\xi = 2\left(\frac{L}{D}\right) \qquad (5)$$

where L is the length, D is the diameter, and V_a is the volume fraction of algae fibers. E_P and E_a are the elastic moduli of the base polymer and algae, respectively. The average length of the algae fiber was ~ 600 μm in most experiments. The diameter of the algal fibers is typically between 50 and 100 μm. By using a mean value of 75 μm for D, ξ can be calculated to be 16. The elastic modulus of the polymer, E_P, can vary significantly depending on formulation and processing conditions.[27] The following procedure was used to estimate E_P. Foams without any algae additions were molded and the elastic modulus in these foams was measured. At a foam density of 30 kg/m³, the elastic modulus in the foam was measured to be 0.15 MPa. Reitz et al.[29] suggested that ϕ in the case of polyurethanes is on the order of 0.9. By using this value in eq. (1) with $\rho_s = 1200$ kg/m³ (typical density of polyurethanes[27]), E_P can be estimated to be on the order of 50 MPa. The elastic modulus of the algal fibers was measured to be between 1 and 5 GPa.[24] Based on these values, η can be calculated to be 0.78 (assuming a mean value of 3 GPa for algal fibers). Hence, E_{CL} and E_{CT} for the solid composite can be obtained as a function of V_a from eqs. (2) and (3). The elastic modulus of
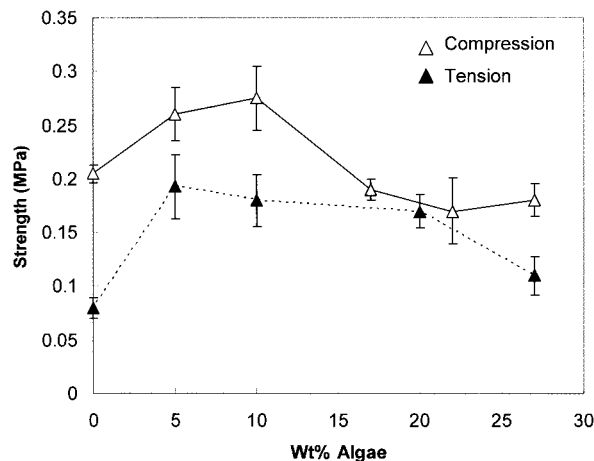

Figure 13 Tensile and compressive strength of polyurethane foams with various amounts of *Cladophora glomerata* algae. In each case, the algae was dried and ground to produce an average fiber length of 600 μm.

the composite foam can then be estimated from the Power law equation:

$$\frac{E_{CL}^*}{E_{CL}} \approx \left(\frac{\rho_c^*}{\rho_{SC}}\right)^{1.6} \qquad (6)$$

and

$$\frac{E_{CT}^*}{E_{CT}} \approx \left(\frac{\rho_c^*}{\rho_{SC}}\right)^{1.6} \qquad (7)$$

where ρ_c^* is the density of the composite foam and ρ_{SC} is the density of the solid composite which can be estimated from the rule of mixtures as

$$\rho_{SC} = \rho_P(1 - V_a) + \rho_a V_a \qquad (8)$$

The calculated values of E_{CT} and E_{CL} for the composite foam with an algae weight fraction of 10% are shown in Figure 12. The measured elastic moduli for various conditions are between the theoretical upper and lower bounds.

The effect of volume fraction algae on the tensile and compressive strength of the composite foam is shown in Figure 13. Up to 30 wt % algae fibers could be added to the isocyanate–polyol mix to produce molded test samples. Peak values of tensile and compressive strengths are obtained between 5 and 10 wt % algae addition. Similar results were reported by Iannace et al.,[22] who added sea algae fibers to biodegradable thermoplastic matrices. The addition of algae to the isocyanate–polyol mix increases the viscosity of the mix. This increase in viscosity may lower the extent of fiber wetting and also affect the bubble nucleation and coalescence. These factors may contribute to the observed reduction in strength beyond 5–10% al-
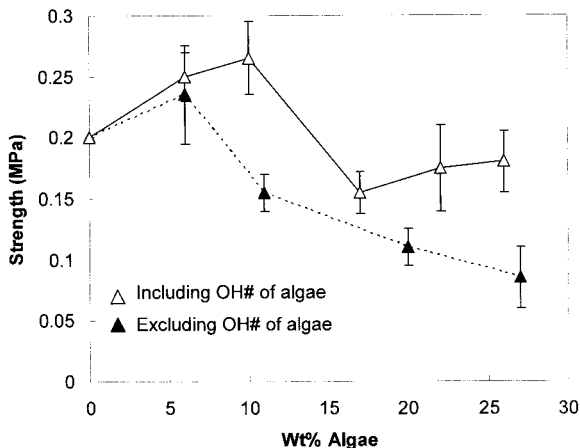
Figure 14 Compressive strength of polyurethane foams as a function of wt % algae. Two different formulations were used to produce the foams. In one case, the weight of isocyanate was calculated without considering the OH# of the algae as shown in eq. (9). The second set of samples was produced with an additional amount of isocyanate to include the OH# of the algae as indicated in eq. (10).

gae. The use of suitable compounding and molding techniques to disperse the fibers may enable higher amounts of algae to be added to the matrix. Iannace et al.[22] have produced composites with 50 wt % algae fibers by compression molding and extrusion. The strength properties of the foam are influenced by the formulation used to prepare the polyurethane as shown in Figure 14. Data for two different formulations are shown in Figure 14. In the first formulation, the algae was considered as an inert filler and the amount of isocyanate was calculated ignoring the hydroxyl groups within the algae as[30]

$$W_{MDI} = \frac{ICIxW_{polyol}xOH\#_{polyol}}{M_{MDI}} \quad (9)$$

where W_{MDI} is the weight of the isocyanate, ICI is the isocyanate index, W_{polyol} is the wight of the polyol, $OH\#_{polyol}$ is the overall hydroxyl number of the polyol blend, and M_{MDI} is the number of moles of isocyanate groups per gram of isocyanate. In the second formulation, the measured hydroxyl number of the algae (300) was included in the formulation and the weight of isocyanate was calculated accordingly:

$$W_{MDI} = \frac{ICI(W_{polyol}xOH\#_{polyol} + W_{algae}xOH\#_{algae})}{M_{MDI}} \quad (10)$$

The data in Figure 14 indicate that the second formulation including the hydroxyl number of the algae yields better mechanical properties than the formulation that does not take the hydroxyl groups of algae into account. It was shown previously that natural polymers (e.g., lignocellulosics) with more than two hydroxyl groups per molecule can be used as polyols during the production of polyurethanes, if the polyol from the natural polymer can be reacted efficiently with the isocyanate.[8] The data in Figure 14 indicate that the hydroxyl groups in the algae can serve as efficient sites for reactions with the isocyanate. Algae can, therefore, be considered as a reinforcing filler in many polyurethanes. Further, if a liquefied polyol can be extracted from the algae, it can serve as a suitable replacement for current polyols, which are obtained primarily from fossil resources.

Molded polyurethane foams typically comprise a low-density foamed core surrounded by a high-density skin of the same material.[31] The properties of the foam depend on skin and core thicknesses and the corresponding densities.[32] The skin thickness for the molded samples in this study varied from 3 to 5 mm. For a sample with a nominal density of 40 kg/m^3, the densities of the skin and the core were on the order of 100–150 and 30 kg/m^3, respectively. This density difference between the skin and core has a significant effect on compressive modulus and strength, as shown in Figure 14. Further, the modulus in the skin and core obeys the Power law relationship described previously:

$$\frac{E^*_{core}}{E^*_{skin}} \approx \frac{0.15}{1.85} \approx \left(\frac{\rho^*_{core}}{\rho^*_{skin}}\right)^{1.6} \approx \left(\frac{30}{150}\right)^{1.6} \quad (11)$$

An analysis of the fracture surface indicates that the fibers at the cell wall exhibit angular tear and are
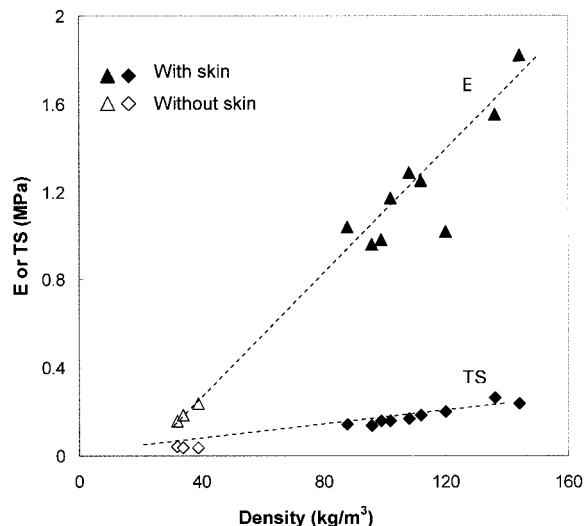

Figure 15 Variation of elastic modulus (E) and tensile strength (TS) in polyurethane foams with 12 wt % algae. Two sets of samples were tested. The first set of samples consisted of molded tensile samples shown in Figure 1. The molded specimens typically consisted of a dense outer skin about 3 mm thick and a much lighter inner core. In the second set, the molded samples were machined to remove a layer of 3 mm from the surface. The tensile properties were measured on the inner core after this skin was removed.
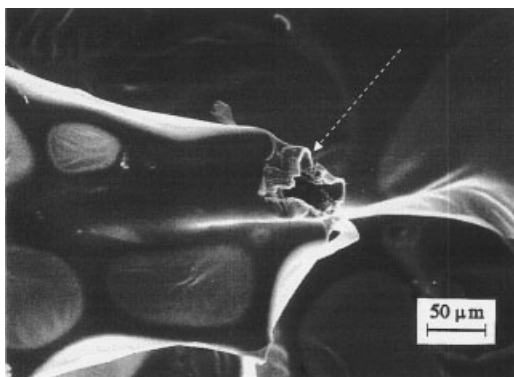
Figure 16 Photograph showing the fracture surface of tensile samples. Note the presence of the fractured algae fiber at the cell walls of the foam (indicated by the arrow). The algae fiber does not appear to have collapsed during the drying of the algal filaments and during the production of the foam.
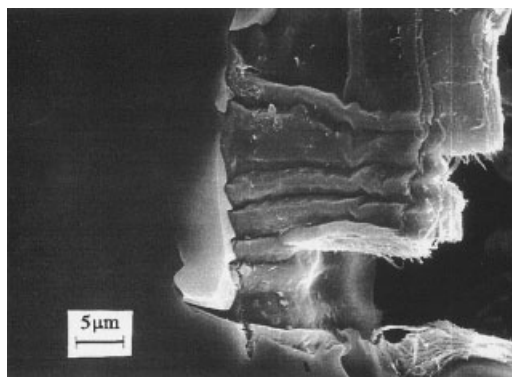

Figure 18 High-magnification photograph showing the fibrillar morphology in the algae fiber exposed on the fracture surface.

thoroughly coated with the polymer (Fig. 16). In addition, the fibers may not collapse during the drying and foaming procedures. In many samples, the internal cell material can also be observed in the exposed fiber (Fig. 17). A typical fibrillar morphology is obtained when the fibers are mechanically loaded, as shown in Figure 18. This fibrillar morphology is consistent with the microcrystalline bandlike cellulose structure that was observed in *Cladophora wrightiana*.[33] The surface of the fibers was not totally clean, indicating relatively good adhesion between the matrix and the fiber.[22]

CONCLUSION

Cl. glomerata is a filamentous green algae with relatively large amounts of highly crystalline microfibrillar cellulose. The filaments exhibit specific modulus and specific strength comparable to most other reinforcing fibers. Depending on the application, wet or dry algae fibers may be used to reinforce polymer

matrices. Dried and chopped filaments were incorporated in a polyurethane matrix to produce a substantial reinforcing effect in the base polymer. The drying process essentially retained the structure in most filaments without significant cell wall collapse. Up to 30 wt % algae could be incorporated into the isocyanate and the resulting mixture could be molded into various shapes. The foams consisted predominantly of a closed cell structure with pore diameters on the order of 500-1000 μm. The fiber length had a significant effect on cell uniformity and foam density. Peak mechanical properties were obtained between 5 and 10 wt % algae. The elastic modulus in the foam exhibits a Power law relationship with foam density, with an exponent of 1.6. The measured mechanical properties of the foam are generally within the limits of the values predicted by models describing the mechanical behavior of composites and cellular solids. The hydroxyl number in the algae was determined to be 300. The hydroxyl groups in the algae can serve as efficient sites for reactions with the isocyanate.
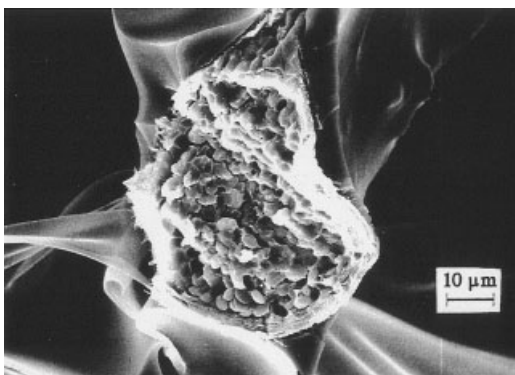

Figure 17 Photograph showing the fractured algae fiber at the cell walls of the foam. Note the internal cellular material in the fractured algae fiber.

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