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Characterization of Surface Modified Flax Fibers and Their Biocomposites with PHB

Seung Goo Lee,[1] *Sung-Seen Choi,*[2] *Won Ho Park,*[1] *Donghwan Cho*[3]

[1] Department of Textile Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea
E-mail: lsgoo@cnu.ac.kr
[2] Research Institute of Advanced Materials, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea
[3] Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Kumi, Kyungbuk 730-701, Korea

Summary: Flax fiber was treated with acetic anhydride or with ethylene plasma to improve adhesion with poly(3-hydroxybutyrate) (PHB). The flax fiber surface became hydrophobic by the surface treatments. The ethylene plasma treated flax fiber has better thermal resistance and shows higher interfacial adhesion strength in flax/PHB biocomposite than the chemically modified flax fiber with acetic anhydride. Optimum conditions of the ethylene plasma treatment were found to be 0.5 cm^3/sec of the ethylene flow rate and 50 W of the plasma power with 5 min of the treatment time.
Keywords: composites; fibers

Introduction

Biocomposite material consists of a biodegradable polymer as matrix and a natural fiber as reinforcing filler. Flax, hemp, jute, ramie, and so on are used as natural reinforcing fibers while derivatives from cellulose, starch, lactic acid, and so forth are used as biopolymeric matrices.[1,2] Both components of the biodegradable polymer and natural fiber are biodegradable but biofibers (natural fibers) do not have necessary thermal stability and good mechanical properties compared to engineering plastics. On the other hand, the best engineering plastics are obtained from synthetic polymers, but they are not biodegradable. Composite materials consisted of natural fibers and non-biodegradable synthetic polymers may offer a new class of materials but are not completely biodegradable. Advantages of natural fibers over traditional reinforcing materials such as glass fiber, talc, and mica are low cost, low density, high toughness, acceptable specific strength properties, reduced tool wear, ease of separation, and enhanced energy recovery as well as biodegradability.

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Natural fibers contain lots of hydroxyl groups which form intramolecular hydrogen bonds and intermolecular hydrogen bonds among other cellulose polymers as well as hydrogen bonds with moisture in the air.[3] Biodegradable polymers may be classified as biosynthetic, semi-biosynthetic, and chemosynthetic types.[4,5] Almost all biosynthetic polymers which are readily available from renewable resources are biodegradable within a reasonable time scale. Many semi-biosynthetic and chemosynthetic polymers are also biodegradable, if they contain chemical bonds which occur in natural compounds. Thus, biodegradability is not only a function of origin but also of chemical structure and degrading environments.

Poly(3-hydroxybutyrate) (PHB), which is commercially produced by a fermentation process with glucose as carbon sources, is biodegradable and has good mechanical properties. Table 1 shows properties of common engineering plastics, polypropylene (PP), poly(ethylene terephthalate), and Nylon-6,6, as well as PHB. Flax fiber as a reinforcing material is eco-friendly and biodegradable, and cost-effective but has improper surface to form strong interfacial bond with polymeric matrix.

Table 1. Properties of PHB and engineering plastics.

Property	PHB	PP	PET	Nylon-6,6
T_m (°C)	180	176	267	265
T_g (°C)	5	-10	69	50
Crystallinity (%)	60-80	50-70	30-50	40-60
Density (g/cm^3)	1.250	0.905	1.385	1.14
Water Absorption (%)	0.2	0.0	0.4	4.5
Modulus (GPa)	3.5	1.7	2.9	2.8
Tensile Strength (Mpa)	40	38	70	83
Elongation at Break (%)	6	40	100	60

Problem in flax-reinforced PHB biocomposite is poor interfacial adhesion due to the different surface chemistries. Flax surface is hydrophilic while PHB has hydrophobic nature. Surface modification of flax fiber is indispensable to improve properties of flax/PHB biocomposite. In the present work, flax was treated with acetic anhydride (acetylation) or with ethylene plasma to reduce its hydrophilicity. The treated flax surface was investigated with FTIR, TGA, SEM, and water contact angle. Interfacial adhesion properties of the modified flax/PHB biocomposite were also investigated.

Experimental

Flax fiber of plain fabric —LN 40 lea was obtained from Samkang Trading Co. of Korea. PHB resin was obtained from Zeneca of UK. The flax fiber was washed with detergent solution at 60 °C for 6 h and then dewaxed with mixture solvent of ethanol/benzene (1/2 of weight ratio) for 3 days at room temperature and finally dried in a convection oven at 80 °C for 24 h. The flax fiber was chemically treated with acetic anhydride (acetylation). The acetylation reactions were performed at 20 °C using 1 g of the dewaxed flax fiber and 6 mL of acetic anhydride containing sulfuric acid as reaction catalyst. The dewaxed flax fiber (1 g) was immersed in glacial acetic acid for 1 h. After filtration, 6 mL of acetic anhydride containing 10 or 20 μL of sulfuric acid was added. The solution was stirred for 5 min. The fibers were washed with aqueous sodium bicarbonate and distilled water and then dried at 60 °C *in vacuo*.

The dewaxed flax fiber was also treated with ethylene plasma. Ethylene (C_2H_4) gas of 99% purity was obtained from Special Gas Co. of Korea. The fiber was pretreated by argon plasma cleaning at power of 100 W and argon flow rate of 0.17 cm^3/sec for 1 min. The plasma powers were 15, 30, 50, 70, and 100 W, the ethylene gas flow rates were 0.17, 0.34, 0.5, 0.67, and 0.84 cm^3/sec, and the treatment time was 5 min.

Morphology of the flax fiber surface was observed with scanning electron microscope (SEM) JSM-5410 of JEOL Co. Water contact angle was measured by dynamic contact angle analyzer (DCA, CHAN 322) at a speed of 500 μm/min. Surface chemical composition was analyzed with FTIR-ATR (FTS-175C of Bio-rad Laboratories Ltd.). Thermogravimetric analysis (TGA) measurement was performed under N_2 condition with a Perkin Elmer TGA-7 at a heating rate of 10 °C/min.

Tensile properties of the flax fiber were measured with an Instron 4467 according to the ASTM D3379 method at a speed of 5 mm/min. Interfacial shear strength between the flax fiber and PHB was measured with micro-debonding test using Instron 4467 w/fixture. The interfacial strength is defined as eq. (1)

$$\sigma = F/\pi Dl \qquad (1)$$

where the σ, F, D, and l indicate the interfacial shear strength, load (gf), diameter of fiber, and embedded length, respectively. PHB knot was made on the flax fiber and the microdroplet was formed by melting the knot at 180 °C for 2 min. The tensile strength was measured with an Instron 4467 at a speed of 0.5 mm/min.

Results and Discussion

Surface of the modified flax fiber was analyzed with FTIR-ATR. Figure 1 shows the FTIR spectra of flax fiber surfaces modified with different methods. A broad band in the region about 3400 cm^{-1} is a characterisctic one of hydrogen bonded O–H stretching vibration. The O–H band of plasma treated flax fiber is slightly sharper than that of untreated one. This may be because some hydroxyl groups (O–H) in the flax fiber are changed to ether groups (O–R, R is alkyl or akenyl) by the ethylene plasma treatment.

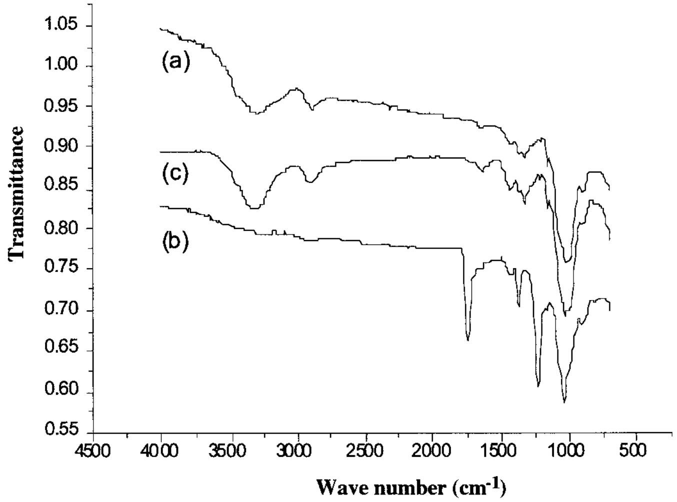

Figure 1. FTIR spectra of differently modified flax fibers: (a) dewaxed fiber; (b) acetylated fiber; and (c) plasma treated fiber (0.5 cm^3/sec and 50 W).

The changed hydroxyl groups result in reduction of intramolecular and intermolecular hydrogen bonds. The O–H peak in the spectrum of acetylated flax fiber is trace. This means that almost hydroxyl groups of the flax fiber are modified by acetylation. A strong sharp peak at 1740 cm^{-1} of the acetylated flax fiber is assigned to carbonyl group (>C=O) stretching vibration. The carbonyl group is formed from acetylation by acetic anhydride as eq. (2). Acetylation has been extensively applied to wood cellulose to stabilize the cell wall and to improve dimensional stability and environmental degradation.[6-8]

$$\text{flax-OH} + CH_3COOCOCH_3 \rightarrow \text{flax-OCOCH}_3 + CH_3COOH \qquad (2)$$

The concentration of sulfuric acid as reaction catalyst affects critically the degree of acetylation. Figure 2 shows the FTIR spectra of acetylated flax fibers with different concentrations of sulfuric acid. The 3400 cm^{-1} peak of acetylated flax fiber with 10 μL of sulfuric acid decreases slightly compared with the untreated fiber.

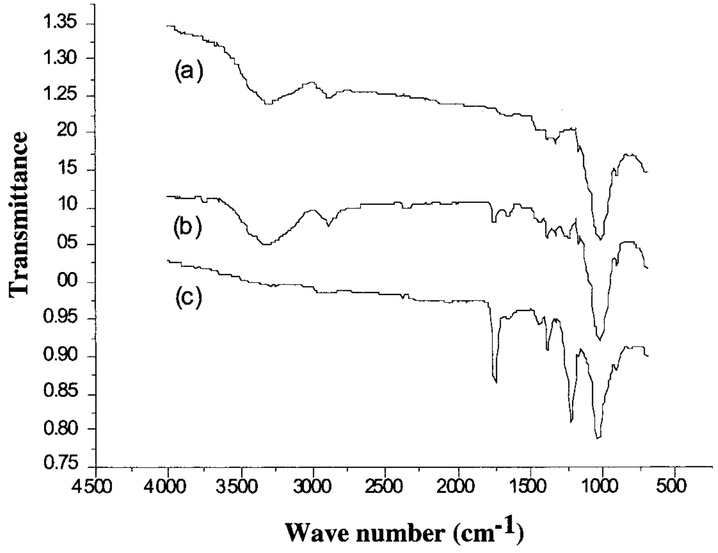

Figure 2. FTIR spectra of acetylated flax fibers with different concentrations of sulfuric acid: (a) untreated fiber; (b) 10 μL of sulfuric acid; and (c) 20 μL of sulfuric acid.

For the acetylated flax fiber with 20 μL of sulfuric acid, the 3400 cm^{-1} peak almost disappears in the spectrum. On the other hand, the 1740 cm^{-1} peak appears in the FTIR spectrum of acetylated flax fiber with 10 μL of sulfuric acid and increases notably in the FTIR spectrum of acetylated flax fiber with 20 μL of sulfuric acid

Figure 3 shows the thermogravimetric curves of modified flax fibers. The acetylated fiber begins to dissociated at lower temperature than the untreated one by over 50°C. This indicates that the acetylated fiber has relatively thermally less stable structure or has lower molecular weight distribution. The larger the molecular weight the higher the degradation temperature when polymers have the same chemical structure. This may be due to etching by acetic acid and breakup of fabric structure by solvent swelling. We believe that crystallinity of the flax fiber will be reduced by solvent swelling and acetylation. Thermal degradation of natural fibers is greatly influenced by their structure and chemical composition.[9-12] On the other hand, the plasma treated flax fiber shows notably improved thermal stability by more than 50°C.

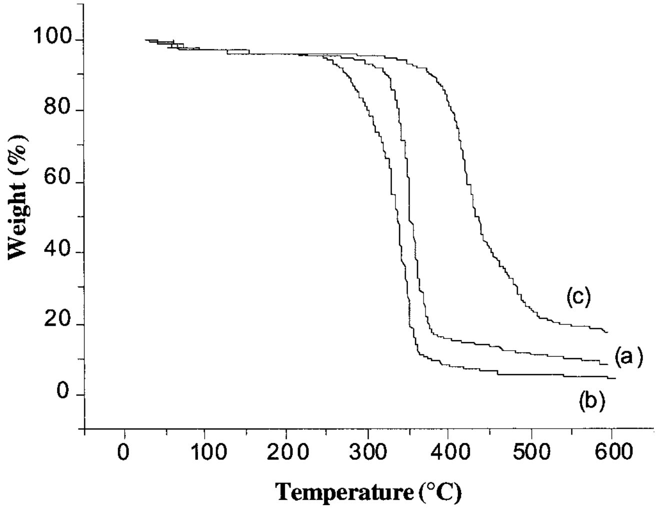

Figure 3. TGA thermograms of differently modified flax fibers: (a) dewaxed fiber; (b) acetylated fiber; and (c) plasma treated fiber (0.5 cm^3/sec and 50 W).

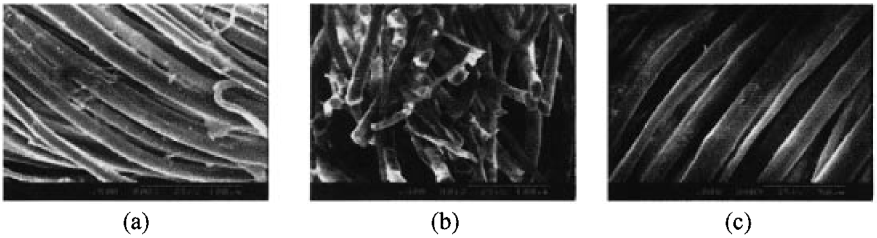
(a) (b) (c)

Figure 4. SEM micrographs of differently modified flax fibers: (a) dewaxed fiber; (b) acetylated fiber; and (c) plasma treated fiber (0.5 cm^3/sec and 50 W).

This may be because some defect points or weak structures of the flax fiber are made up by the ethylene plasma treatment. The plasma treated fiber surface is smoother than the untreated one. Figure 4 shows the microphographs of modified flax fibers. The acetylated flax fiber has some cracks, which leads to poorer thermal stability. The plasma treated fiber has smoother surface than the untreated one.

The water contact angles of the surface modified flax fibers are larger than that of untreated one (Figures 5 and 6). For the ethylene plasma treated flax fibers the water contact angle becomes, on

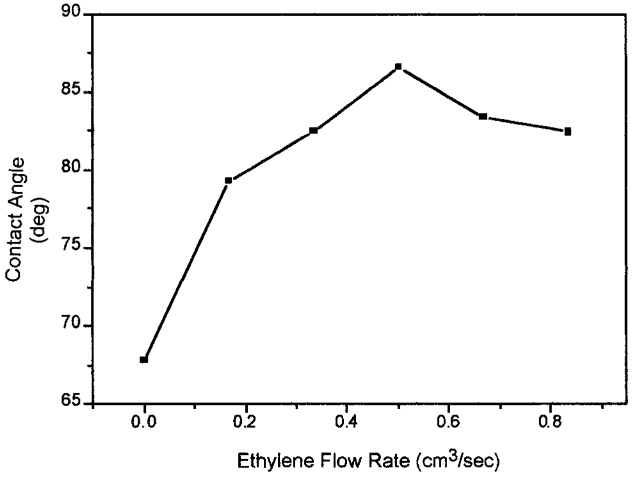

Figure 5. Variation of water contact angle of the plasma treated flax fiber with the ethylene flow rate (50W and 5min). Water contact angle of the acetylated flax fiber is 79°.

the whole, larger with increase of the ethylene flow rate as well as the plasma power. This is due to induction of aliphatic and acetic moieties on the flax fiber by the plasma and acetylation treatments, respectively. The contact angles of plasma treated flax fibers are larger than that of acetylated one. The contact angles of untreated, acetylated, and plasma treated (0.5 cm^3/sec and 50 W) flax fibers are 67.8, 79.0, and 86.6°, respectively.

The contact angle measurements indicate that the surface of the samples treated with ethylene plasma is more hydrophobic than that of acetylated fibers. These data suggest that the hydroxyl groups evidenced by the IR spectrum of plasma treated fibers (Figure 1) are not present on the sample surface but only in the bulk material.

Tensile properties of the flax fibers are summarized in Table 2. Tensile strength and modulus of the plasma treated fiber are nearly the same to the untreated one, while those of the acetylated one are lower than those of the untreated one. This is an evidence that the acetylated flax fiber has to some extent destroyed structure compared with the untreated one. On the other hand, the plasma treatment does not damage the flax fiber structure.

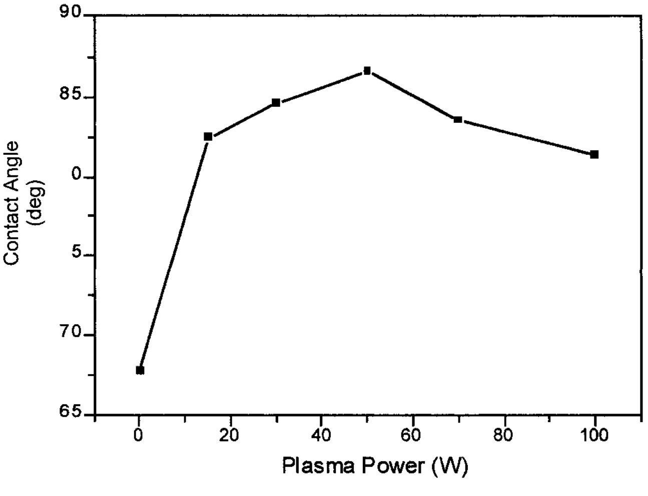

Figure 6. Variation of water contact angle of the plasma treated flax fiber with the plasma power (ethylene flow rate 0.5 cm^3/sec and treatment time of 5 min). Water contact angle of the acetylated flax fiber is 79°.

Table 2. Tensile properties of differently modified flax fibers.

Fiber	Dewaxed	Acetylated	Plasma Treated (0.5 cm^3/sec and 50 W)
Tensile Strength (gf/mm^2)	21.8	20.1	22.4
Tensile Modulus (gf/mm^2)	162	145	160.5

Figure 7 and 8 show variations of the interfacial shear strength between the plasma treated fiber and the PHB matrix with the ethylene flow rate and with the plasma power, respectively. The interfacial shear strength increases sharply at the ethylene flow rate of 0.17 cm^3/sec and then slightly increases or does not change notably. The interfacial shear strength increases sharply with increase of the plasma power until 50 W and then decreases. The interfacial shear strength of plasma treated fiber are, on the whole, stronger than that of acetylated one.

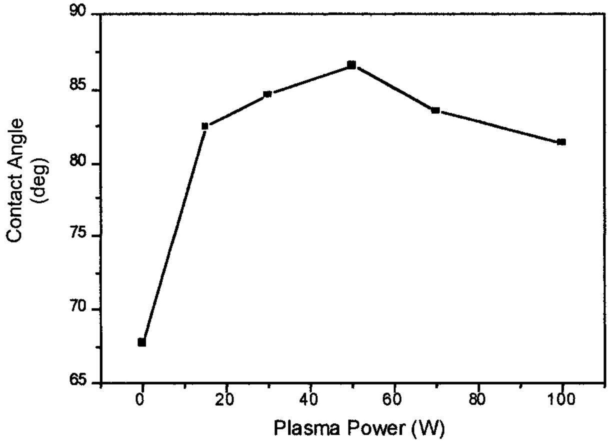

Figure 7. Variation of interfacial shear strength of the plasma treated flax fiber-filled PHB composite droplet with the ethylene flow rate (plasma power of 50 W and treatment time of 5 min). Interfacial shear strength of the acetylated flax fiber is 10.3 MPa.

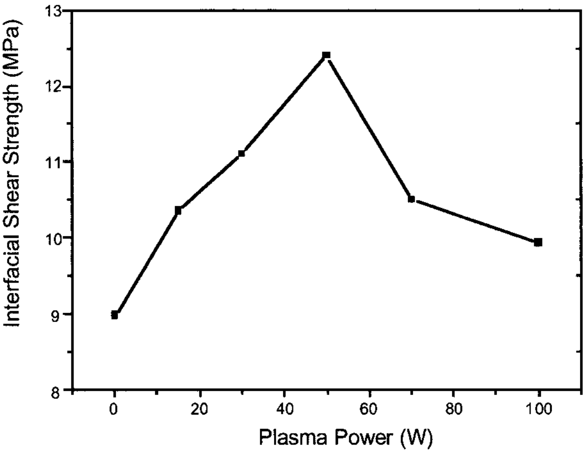

Figure 8. Variation of interfacial shear strength of the plasma treated flax fiber-filled PHB composite droplet with the plasma power (ethylene flow rate 0.5 cm^3/sec and treatment time of 5 min). Interfacial shear strength of the acetylated flax fiber is 10.3 MPa.

The interfacial shear strengths of untreated, acetylated, and plasma treated (0.5 cm^3/sec and 50 W) flax fibers are 8.8, 10.3, and 12.4 MPa, respectively. This may be also due to uneven surface of the acetylated flax fiber. Figure 9 shows the micrographs of interfacial fractures after the micro-debonding test.

Conclusions

Flax fiber surface was successfully modified by ethylene plasma treatment and acetylation. Aliphatic and acetic moieties were induced on the flax fiber surface by plasma and acetylation treatments, respectively. The plasma treatment with ethylene brought about the higher thermal resistance and larger interfacial strength in flax/PHB biocomposite than the chemical modification by acetic anhydride without damage to flax fiber. Optimum condition for ethylene plasma treatment of flax fiber was obtained at ethylene flow rate of 0.5 cm^3/sec, plasma power of 50 W, and plasma time of 5 min.

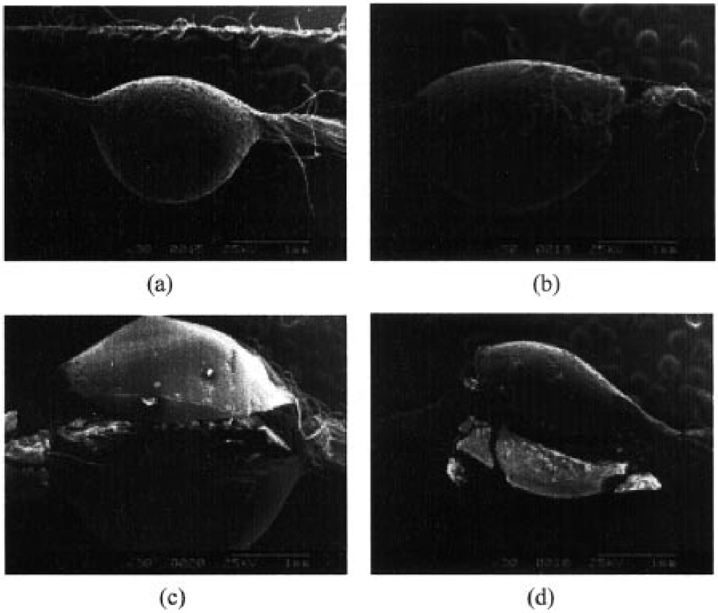

Figure 9. SEM micrographs of interfacial fractures of the PHB composite droplets filled with differently modified flax fibers: (a) before the test; (b) dewaxed fiber; (c) acetylated fiber; (d) plasma treated fiber (0.5 cm^3/sec and 50 W).

Acknowledgment

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