Materials Physics and Mechanics 11 (2011) 1-8 Received: December 19, 2010

MECHANICAL PROPERTIES OF HEMP FIBERS AND HEMP/PP COMPOSITES: EFFECTS OF CHEMICAL SURFACE TREATMENT

N.P.G. Suardana[1,2], Yingjun Piao[2], Jae Kyoo Lim[2]*

[1] Mechanical Engineering Department, Udayana University, Kampus Bukit Jimbaran 80361, Bali Indonesia

[2] Department of Mechanical Design Engineering, Automobile Hi-Technology Research Institute, Chonbuk National University, Deokjin 1-664-14, Jeonju, 561-756, Republic of Korea

* e-mail: jklim@chonbuk.ac.kr

Abstract. The effects of chemical surface treatment on the hemp fibers and mechanical properties of hemp fiber composites were investigated. After chemical treatment of the fibers, the density and weight loss were measured. The surface morphologies of fibers were observed using SEM, and FT-IR was utilized to characterize the chemically modified fibers. Among the tested samples, the 4 wt.% NaOH-treated fiber composites demonstrated the best mechanical properties. The fracture surfaces of the composites were also observed by SEM.

1. Introduction

Synthetic polymer composite materials are currently widely used in many industrial areas to meet light-weight and high strength requirements. However, with the increasing amount of synthetic polymer materials present worldwide, environmental issues such as disposal treatment, waste disposal services, and incineration pollution are becoming increasingly important [1,2].

There are two basic types of fibers: natural fibers and synthetic fibers. Many researchers have studied composites based on these fibers [3-5]. Compared with synthetic fibers, the advantages of using natural fibers in composites are their low cost, low density, unlimited availability, biodegradability, renewability, and recyceability [6-11]. Some studies suggest that natural fibers have the potential to replace glass fibers in polymer composite materials [12-14]. They have already found uses in building, construction, automotive, and packaging applications. For example, vehicle interior parts such as door trim panels made from natural fiber-polypropylene (PP) and exterior parts such as engine and transmission covers from natural fiber-polyester resins are already in use [15].

Some of the problems associated with untreated natural fiber-reinforced thermoplastic composites include poor interfacial adhesion between the cellulose fibers and the thermoplastic matrix, limited thermal stability of the composites and poor fiber separation and dispersion within the composites [16]. All plant-derived cellulose fibers are polar and hydrophilic in nature, mainly as a consequence of their chemical structure. Poly-olefins such as polypropylene, on the other hand, are largely non-polar and hydrophobic. The incompatibility of the polar cellulose fibers and the non-polar thermoplastic matrix leads to poor adhesion, which then results in a composite material with poor mechanical properties [17]. However, these drawbacks can be overcome by fiber treatment.

The hemp plant, in particular, produces high quality natural fibers that are inexpensive

and exhibit excellent mechanical properties when compared to other natural fibers. Therefore, they are used in the automobile industry, mostly as interior components [18, 19].

In this paper, the effects of chemical surface treatment on the fiber surface morphology and mechanical properties of hemp/PP composites were investigated. The effects of two different surface treatments at various concentrations on the hemp fibers were evaluated by density, weight loss, surface morphology, FTIR, and tensile property measurements. Composites were produced from untreated and treated fiber-reinforced polypropylene and the effects of fiber treatment on their mechanical properties were analyzed.

2. Experimental methods

Materials. The hemp used in this study was produced in the Hubei province of China. Table 1 and Figure 1 show the chemical composition and bundle of the hemp fibers, respectively. This composition plays an important role in influencing the characteristic of the fibers. Hence, the composition may affect the properties of the composites.

The fibers were washed with water to remove dust and ash. Then, the hemp fibers were sterilized in boiling distilled water in an oven maintained at 100 ℃ for 1 h. After these processes, the fibers were rinsed in tap water and then dried in an oven at 70 ℃ for 12 h.

The total length of the fibers was about 2,500 mm and they were cut into short fibers, 5-10 mm in length, by scissors.

Table 1. The chemical composition of hemp fibers [19,20].

	Cellulose	Pectin	Hemicelluloses	Lignin	Waxes and oils
wt.%	70.2-76.12	0.9-1.55	12.28-22.4	3.7-5.7	0.8-1.59

Fig. 1. Photograph of a hemp bundle.

Surface treatment. The effect of surface treatment of natural fibers on their properties are usually functions of the type and concentration of the treatment solution used [21]. The chemicals used in this study were sodium hydroxide (NaOH; Showa Chemical Co. LTD.) and silane coupling agent (LD5701, DAMI Co. LTD). Sodium hydroxide (NaOH) and silane were used in this study to performance the surface treatment on the hemp fibers at different solution concentrations. To evaluate the effect of the sodium hydroxide concentrations, the hemp fibers were treated using 2%, 4%, and 6% sodium hydroxide solution. The fibers were submerged in the sodium hydroxide solution for 1h at oven 95 ℃. The fibers were then rinsed with tap water to eliminate any NaOH solution sticking to the fiber surface and dried in an oven at 70 ℃ for 24 h. The silane coupling agent used was a γ-glycidoxypropyltrimethoxy-silane with the chemical constitution of $H_2COCHCH_2O(CH_2)_3Si(OCH_3)_3$. The treatment involved the use of 2, 4, and 6 wt.% solution of the silane coupling agent, where the same procedure that was used for Sodium hydroxide was implemented.

Sanning electron microscopy (SEM). The surface morphologies of untreated fibers,

NaOH treated fibers, silane coupling agent treated fibers, and the fracture surfaces of the tensile composite specimens were coated with gold and then examined using a scanning electron microscope (SEM) (Jeol JSM-6400 Japan).

Infra-red analysis. The IR spectra of fiber samples (4,000-400 cm^{-1}) were recorded using a FTIR spectrometer (Perkin Elmer). Before testing, a powder of the fiber samples was mixed with KBr powder and cold-pressed into a suitable disk for FTIR measurement.

Fabricate hemp/PP composite plate. The PP film was cut into a 180 mm × 155 mm sheet. The short hemp fibers and PP film were uniformly and homogeneously placed into the mold, layer by layer. Then, the mold was placed onto a hot press machine (Standard Presses, No.3968, Carver, Inc.). The subsequent hot-pressing was performed at 200 ℃ under a pressure of 1.3 MPa for 15 min. The mold was removed from the hot press machine and cooled down to room temperature in the cooling-press with a load of 0.3 MPa. The volume fraction of fibers was 30% in all composite plates.

Mechanical property tests. The tensile test and flexural tests were conducted according to ASTM standard testing methods D3039 and D790-03, respectively. The tests were conducted on a universal material testing machine (Instron 4206) a 750 kgf load cell at a crosshead speed of 3 mm/min at room temperature.

3. Results and Discussion

Table 2 shows the density, weight loss and tensile strength of untreated and surface-treated hemp fibers. The fiber density was measured according to ASTM D 3800-99. When the concentration was increased, the density of the alkali and silane-treated hemp fibers decreased. The alkali-treated hemp fibers had the highest weight loss values. The alkali treatment removed the lignin, pectin, hemicellulose, ash, and resulted in some extraction during the process [22], which is the main cause of the weight loss. After silane treatment, the weight of the fibers increased slightly.

Table 2. The density, weight loss and tensile strength of hemp fibers after treatments.

Hemp fiber	Untreated	NaOH			Silane		
		2%	4%	6%	2%	4%	6%
Density(g/cm^3)	1.249	1.203	1.160	1.127	1.216	1.170	1.150
Weight loss (%)		-7.99%	-9.78%	-13.58%	+0.6%	+1.08%	+2.17%
σ_t (MPa)	962.5	905.63	866	670.75	976.67	986	1025.2

SEM observation of single fibers. NaOH-treated hemp fibers. Untreated fibers were covered with a membrane layer (pellicle). After NaOH treatment, the membrane was removed. As the NaOH concentration increased, nearly the entire membrane was removed from the surface of the fiber and the diameter decreased. From Fig. 2a, it is seen that the surface of an untreated hemp fiber is covered with a layer of substances, which may include pectin, lignin, and other impurities. After NaOH treatment (Fig. 2b-d), most of the lignin and pectin are removed resulting in a rougher surface with some fibrils [22-24]. Therefore, the tensile strength of single hemp fibers decreased after alkali treatment when the alkali concentration increased (Table 2).

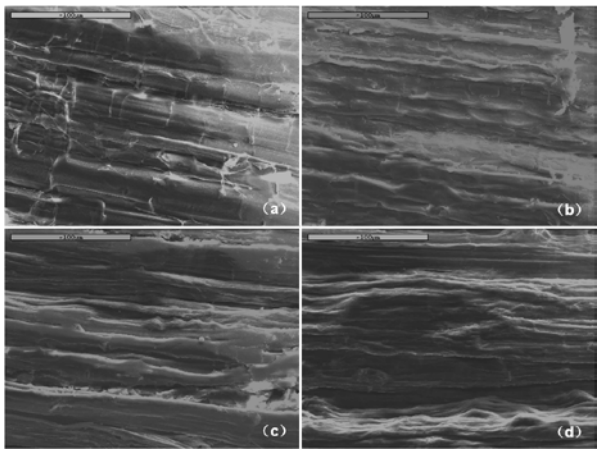

Fig. 2. SEM images of the surfaces of (a) untreated, (b) 2% NaOH-treated, (c) 4% NaOH-treated, and (d) 6% NaOH-treated hemp fibers.

Figure 3 shows SEM images of the hemp fibers before and after the silane treatment. There were significant differences in the fiber morphologies after NaOH treatment and silane treatment as the fibers were coated with silane after treatment with silane. A similar result was obtained with henequen fibers by Gonzalez et al. [25], in which after silane treatment, silane was effectively deposited on the fiber surface and there was no dramatic change in the surface morphology as compared to alkali treated. Table 2 shows that the tensile strength of the hemp fibers increased as the silane concentration was increased.

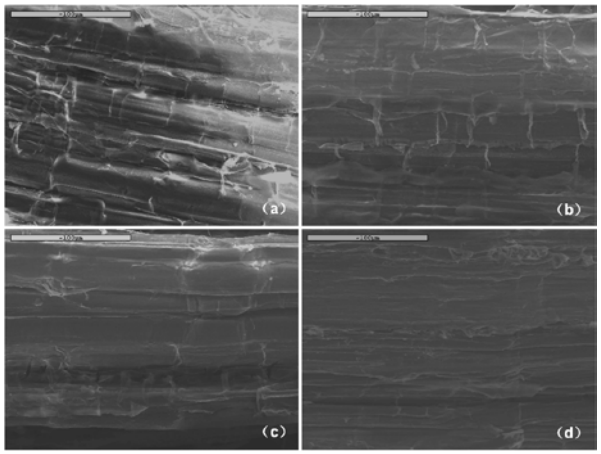

Fig. 3. SEM images of the surfaces of (a) untreated, (b) 2% silane-treated, (c) 4% silane-treated, and (d) 6% silane-treated hemp fibers.

FTIR analysis of single fibers. The FTIR spectra of the untreated and chemically modified fibers are shown in Fig. 4 and Fig. 5. Figure 4 shows the FTIR spectra of untreated, alkali-treated (2%), alkali-treated (4%), and alkali-treated (6%) fibers. The spectra show many transmittance bands. The CH stretch at 2919 cm^{-1} is present in all fibers. The C=O (carbonyl) peak at 1732 cm^{-1} slightly disappeared when the alkali treatment concentration was increased and totally disappeared at 6 wt.% NaOH because of the removal of the reducible hemicelluloses from the fiber surfaces [25]. Also, the peak at 1240 cm^{-1} reduced when the alkali concentration was increased. This peak is a C-O stretching of the acetyl groups of lignin. Lignin is partially removed from the hemp fiber surface after alkali treatment [26]. Figure 5 shows the FTIR spectra of the untreated, silane-treated (2%), silane-

treated (4%), and silane-treated (6%) hemp fibers. After silane treatment, peaks should be present at 766 and 847 cm^{-1} [27]. However, the FTIR spectra do not clearly show the effect of silane on the transmittance bands. This may be due to the reaction between the silane and chemical components are weak, such that the silane concentration on the hemp fiber surfaces is too small to be detected by FTIR [22].

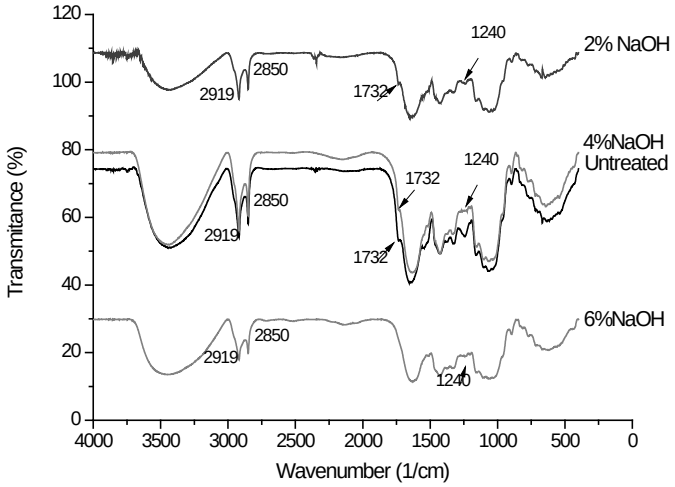

Fig. 4. Spectra of the untreated and NaOH-treated hemp fibers.

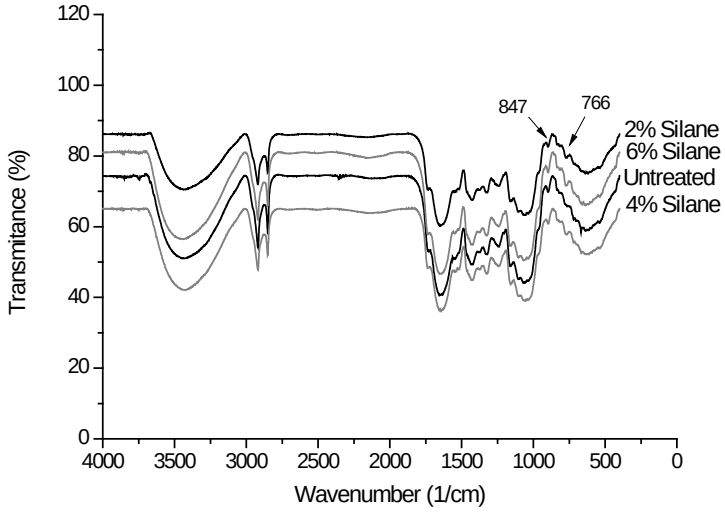

Fig. 5. Spectra of the untreated and silane-treated hemp fibers.

Mechanical properties of the composites. The tensile and flexural strengths of the hemp fiber-reinforced PP composites are shown in Fig. 6. The tensile strength of the untreated hemp/PP composites is almost the same as the neat PP. After NaOH treatment, the tensile strengths of composites were higher than the untreated fiber composite. Figure 6a shows that the 4% alkali-treated fiber composite demonstrated the highest tensile and flexural strength values. The trend of the flexural strengths of NaOH-treated fiber composites is similar to the tensile strength trend. Meanwhile, the tensile and flexural strengths of the 6% NaOH-treated fiber composite are lower than the 2% and 4wt% NaOH-treated composites. This may be due to the hemicelluloce and lignin present on the fiber, which was substantially

removed after the 6% alkali treatment causing fibril in the fiber to be easily pulled out (fibrillation). This explanation is supported by the SEM observation (Fig. 7d), which shows the fibril pullout. Different from the NaOH treatment, the tensile and flexural strengths of the silane-treated composites (Fig. 6b) are nearly equal to those of the untreated hemp fiber/PP composites. This demonstrates that the silane treatment does not affect on the mechanical properties of the composites.

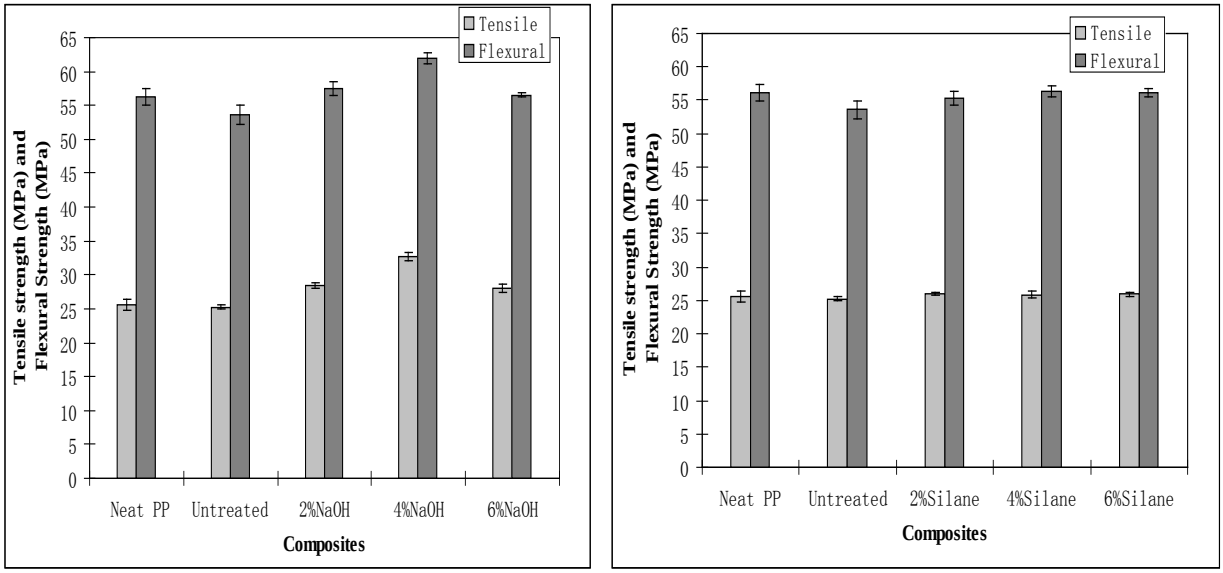

Fig. 6. Tensile and flexural strengths of a) alkali and b) silane-treated hemp fiber-reinforced PP composites.

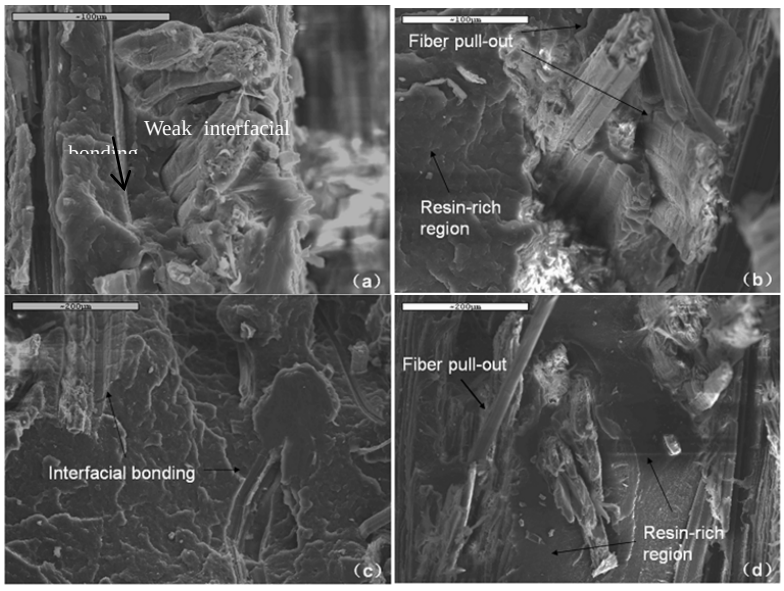

Fig. 7. SEM observations of tensile fracture surfaces of the (a) untreated fiber composites, (b) 2% NaOH-treated fiber composites, (c) 4% NaOH-treated fiber composites, and (d) 6% NaOH-treated fiber composites.

SEM micrographs of the hemp/PP composites with different surface treatment concentrations are shown in Fig. 7 and Fig. 8. From Fig. 7a, it was demonstrated that the interfacial bonding between the untreated hemp fiber and PP resin is not good, as indicated by

the gap between them. This may be attributed to the low adhesion between the fiber surfaces and PP resin. Hence, the tensile strength of this composite is low. NaOH treatment can remove the thin membrane from the surface of the fibers, resulting in improved adhesion with the PP resin (see Fig. 7b-7d). After NaOH treatment, the interfacial bonding between the hemp and PP is much better than in the untreated hemp fiber composite. The 4 wt.% NaOH-treated fiber composite demonstrated the maximum tensile and flexural strength values because the best interfacial bonding occurred in this composite. Figure 8 shows the fracture surface of the silane-treated hemp fiber composites where most of the hemp fiber and PP lack interfacial bonding. Therefore, the silane treatment does not affect the mechanical properties of the composites.

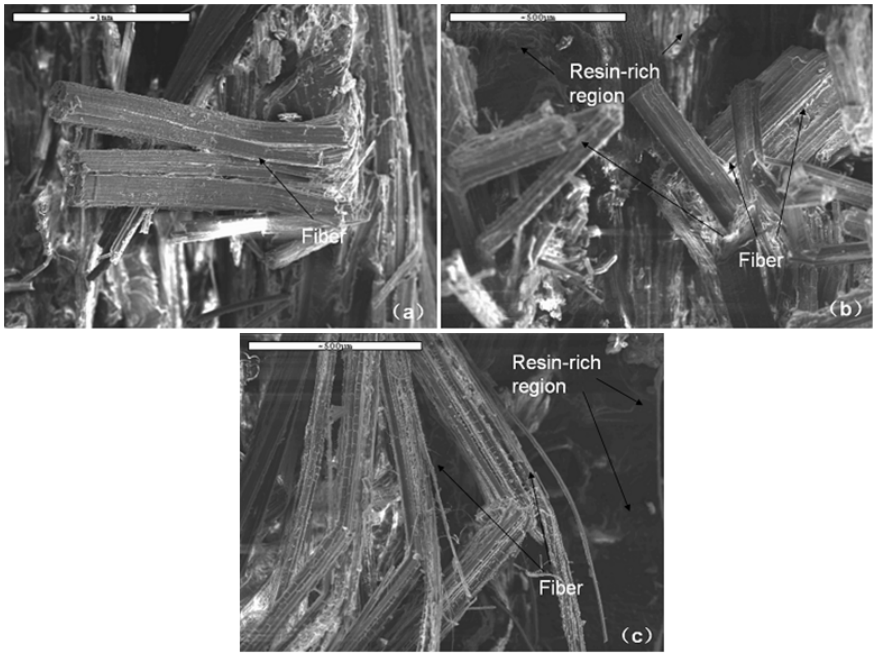

Fig. 8. SEM observations of tensile fracture surfaces of the (a) 2% Silane-treated fiber composites, (b) 4% Silane-treated fiber composites, and (c) 6% Silane-treated fiber composites.

4. Conclusions

Alkaline treatment decreased the density and tensile strength but increased the weight loss of hemp fibers as alkali treatment removes the reducible hemicelluloses and lignin from the fiber surfaces. Moreover, silane treatment decreases the density but increases the weight and tensile strength of hemp single fiber due to the silane coating on the fiber surface. The effects of alkali and silane treatments on hemp fibers were also investigated by SEM and FTIR analyses. The alkaline treatment of hemp fiber increased the tensile and flexural strengths of hemp/PP composites, indicating that interfacial bonding improved after alkaline treatment. The best tensile and flexural strengths of the hemp reinforced PP composites were achieved with the 4% alkali chemical treatment. Meanwhile, the tensile and flexural strengths of the 6% NaOH-treated fiber composite were lower than those of the 2% and 4 % NaOH-treated composites. This result may be due to the presence of hemicelluloce and lignin on the fiber, which was mostly removed after the 6% alkali treatment which caused fibrils in the fibers to be easily pulled out (fibrillation). This explanation is supported by SEM observations. As opposed to the NaOH treatment, the tensile and flexural strengths of the silane-treated composites were nearly equal to those of the untreated hemp fiber/PP composites. Therefore,

the silane treatment of the hemp fibers does not affect the mechanical properties of the composites.

Acknowledgement
The first author is grateful to the Ministry of National Education of the Republic of Indonesia for supporting his program at Chonbuk National University, Korea.

References
[1] J. Jayaramudu, A.V. Rajulu, B.R. Guduri // *J. Reinf. Plastics and Compos.* **29** (2010) 1006.
[2] S.S. Ray, M. Okamoto // *Macromolecular Rapid Communications* **24** (2003) 815.
[3] Y.J. Kim, J.K. Lim // *KSME Inter. J.* **15** (2001) 1380.
[4] N. Chand, P.K. Rohatgi, *Natural Fibres and Their Composites* (Periodical Experts Book Agency, New Delhi, 1994).
[5] PJ.H. Franco, A.V. Gonzalez // *Compos. Part B* **36** (2005) 597.
[6] P.V. Joseph, M.S. Rabello, L.H.C. Mattoso, K. Joseph, S. Thomas // *Compos. Sci. Technol.* **68** (2002) 1357.
[7] A.C.N. Singleton, C.A. Baillie, P.W.R. Beaumont, T. Peijs // *Compos. Part B* **34** (2003) 519.
[8] A. Espert, F. Vilaplana, S. Karlsson // *Compos. Part A* **35** (2004) 1267.
[9] Y. Li, Y-W. Mai, L. Ye // *Compos. Sci. Technol.* **60** (2000) 2037.
[10] D. Ray, B.K. Sarkar, S. Das, A.K. Rana // *Compos. Sci. Technol.* **62** (2002) 911.
[11] A.K. Bedzki, J. Gassan // *Progress in Poly. Sci.* **24** (1999) 221.
[12] N.E. Zafeiropoulos, D.R.Williams, C.A. Baillie, F.L.Matthews // *Compos. Part A: Appl. Sci. Manuf.* **33** (2002) 1083.
[13] J. Gassan, A.K. Bledzki // *Appl. Compos. Mater.* **7** (2002) 373.
[14] S.V. Joshi, L.T. Drzal, A.K. Mohanty, S. Arora // *Compos. Part A* **35** (2004) 371.
[15] S. Panthapulakkal, M. Sain // *J. Appl. Poly. Sci.* **103** (2007) 2432.
[16] G.W. Bechermann, K.L. Pickering // *Compos. Part A* **39** (2008) 979.
[17] D. Maldas, B.V. Kokta // *Inter. J. Poly. Mater.* **27** (1994) 77.
[18] R.H. Hu, J.K. Lim, In: *Proceedings of 2005 International Conference on Mechanical and Automobiles* (Jeonju, Korea, 2005), p. 255.
[19] D. Sedan, C. Pagnoux, T. Chotard, A. Smith, D. Lejolly, V. Gloaguen, P. Krausz // *J. Mater. Sci.* **42** (2007) 9336.
[20] M. Kostic, B. Pejic, P. Skundric // *Biores. Technol.* **99** (2008) 94.
[21] M.Z. Rong, M.Q. Zhang, Y. Liu, G.C. Yang, H.M. Zeng // *Compos. Sci. Technol.* **61** (2001) 1437.
[22] N. Sgriccia, M.C. Hawley, M. Misra // *Compos. Part A: Appl.Sci.Manuf.* **39** (2008) 1632.
[23] L.Y. Mwaikambo, M.P. Ansell // *J. Appl. Poly. Sci.* **84** (2002) 2222.
[24] H. Gu // *Mater. Design* **30** (2009) 3931.
[25] A.V. Gonzalez, J.M. Cervantes-Uc, R. Olayo, P.J. Herrera-Franco // *Compos. Part B* **30** (1999) 309.
[26] W. Liu, A.K. Mohanty, L.T. Drzal, P. Askel, M. Misra // *J. Mater. Sci.* **39** (2004) 1051.
[27] M.A. Khan, L.T. Drazal // *J. Adhesion Sci. Technol.* **18** (2004) 381.