Effect of γ-Aminopropyl Trimethoxy Silane on the Performance of Jute–Polycarbonate Composites

Mubarak A. Khan,[1] M. Masudul Hassan[2]

[1]Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, Dhaka, Bangladesh
[2]Department of Chemistry, MC College of Bangladesh National University, Sylhet-3100, Bangladesh

ABSTRACT: The composites of jute fabrics (hessian cloth) and polycarbonate were prepared by compression molding. The jute surface was modified with γ-aminopropyl trimethoxy silane (Z-6011) to improve interfacial adhesion between jute and polycarbonate. The treated and untreated jute surfaces as well as composites were investigated by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, Environmental scanning electron microscopy, Dynamic mechanical analysis, and mechanical testing. XPS and FTIR assure that the silane plays important role to form interfacial bonding with the jute fibers and polycarbonate. The surface topography of silanized and virgin fibers, and the interfacial adhesion properties of the composite were investigated by ESEM. DMA analysis shows the improved storage and loss moduli of silanized jute composite as compared to the untreated one. The modified jute composite also produces enhanced mechanical properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4142–4154, 2006

Key words: jute; natural fiber; polycarbonate; composite; amino-silane; XPS

INTRODUCTION

The properties and the performance of composites depend on the properties of the individual components and their interfacial adhesion. In general, fibers are the principal load-bearing materials, while the surrounding matrices keep them in the desired location, and orientation acts as the load transfer medium between them and protects them from environmental damage. Surface properties of fibers must be modified accordingly to ensure appropriate interfacial interaction. The interest in using natural fibers such as different plant fibers as reinforcement in plastics has increased dramatically during the last few years. Owing to environmental conditions, it would be very interesting if natural fibers could be used instead of traditional glass and carbon fibers in different applications. Glass fibers can not only cause health problems but also leave residues after the use of composites with high glass fiber content and are difficult to recycle due to low energy values. Natural fibers are more advantageous over man-made fibers due to their low weight, recycle-ability, and biodegradability. They are renewable raw materials having high strength and stiffness and cause no skin irritation.[1–4] The most important disadvantage of natural fiber is its high level of water uptake, while other disadvantages are quality variations and low thermal stability. Owing to these limitations of the jute fiber to act as reinforcing materials, its commercial application in fiber-reinforced composite has not gained much success. Therefore, an attempt has been made to overcome these drawbacks through chemical modification with silane coupling agents. The use of silanes as coupling agents in reinforced polymer composites of natural fiber is analogous to that of synthetic fiber. The large-scale commercial availability of silanes with a variety of reactive functional groups has led to the development of new bonding technologies for organic materials.[5,6] The objective of the present work is to study the chemical modification of jute fiber with silane coupling agent for improving its suitability as a reinforcing material in the performance of jute–polycarbonate (PC) composites which were then characterized by various experimental techniques.
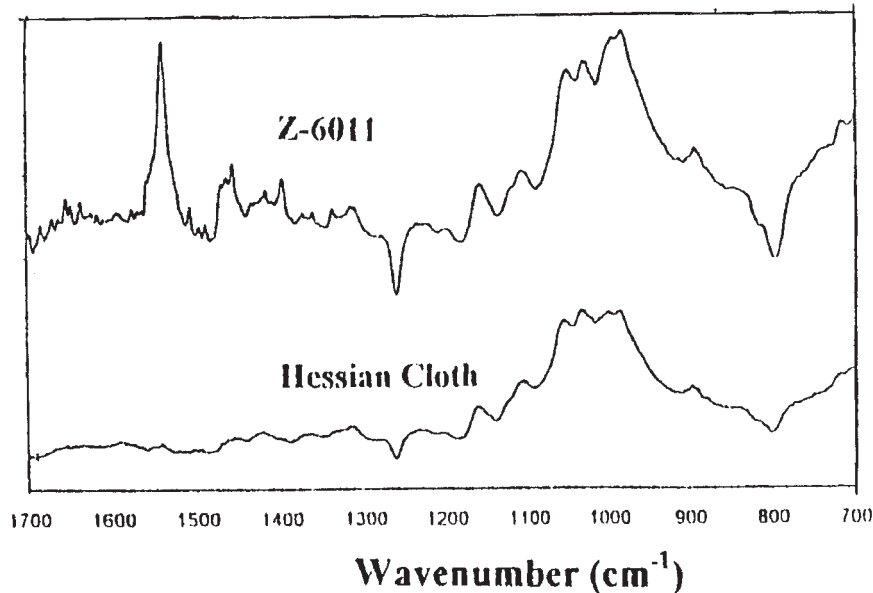
EXPERIMENTAL

Materials

Polycarbonate (PC) sheets (8040, FDA grade) of different thicknesses were purchased from G. E. Company, USA. γ-Aminopropyl triethoxy silane (Z-6011) as an amino-silane coupling agent was procured from Dow Corning, USA. Bleached jute fabric (hessian cloth) was supplied by the Bangladesh Jute Research Institute (BJRI), Dhaka, Bangladesh.
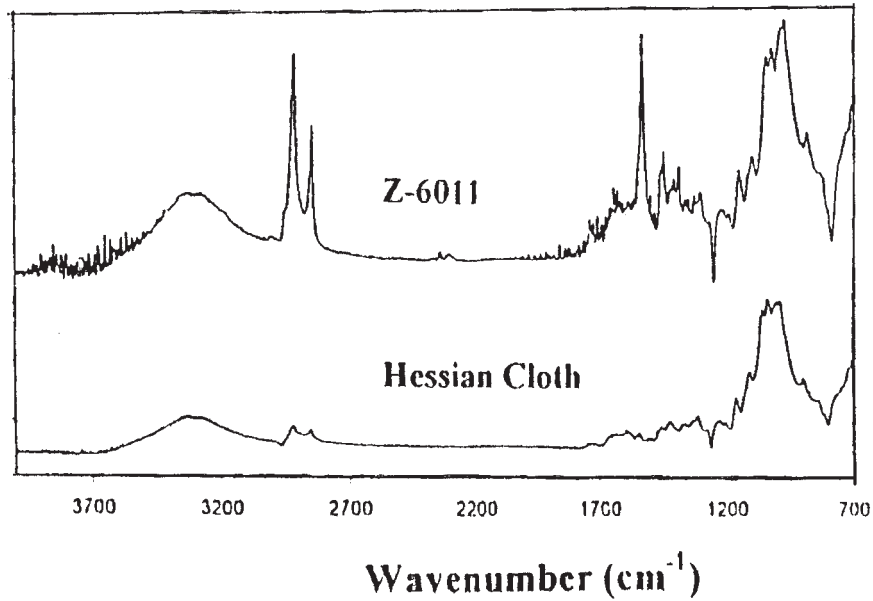
(a)

(b)

Figure 1 FTIR spectra from 4000–700 cm^{-1}(a) and 1800–700 cm^{-1} (b) of untreated and silanized jute.

Methods

Surface treatment

Silane (1% w/w) solution in methanol was prepared and the pH value of the solution was adjusted to 3.5 with the addition of acetic acid. After the continuous stirring of the solution for 10 min, the hessian cloth (HC) was immersed in it for 6 h and then dried in ambient temperature.

Composite fabrication

Composites of PC and HC were prepared by sandwiching three layers of HC placed alternately between
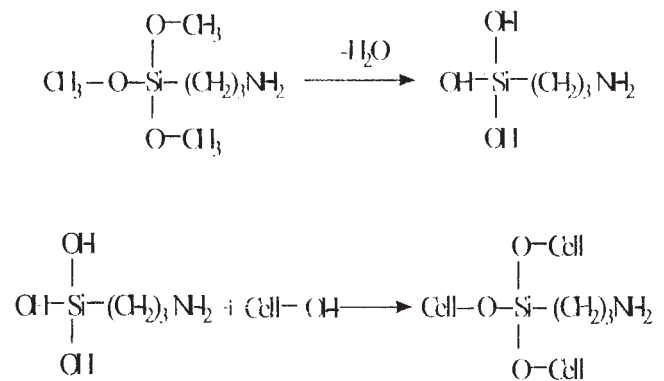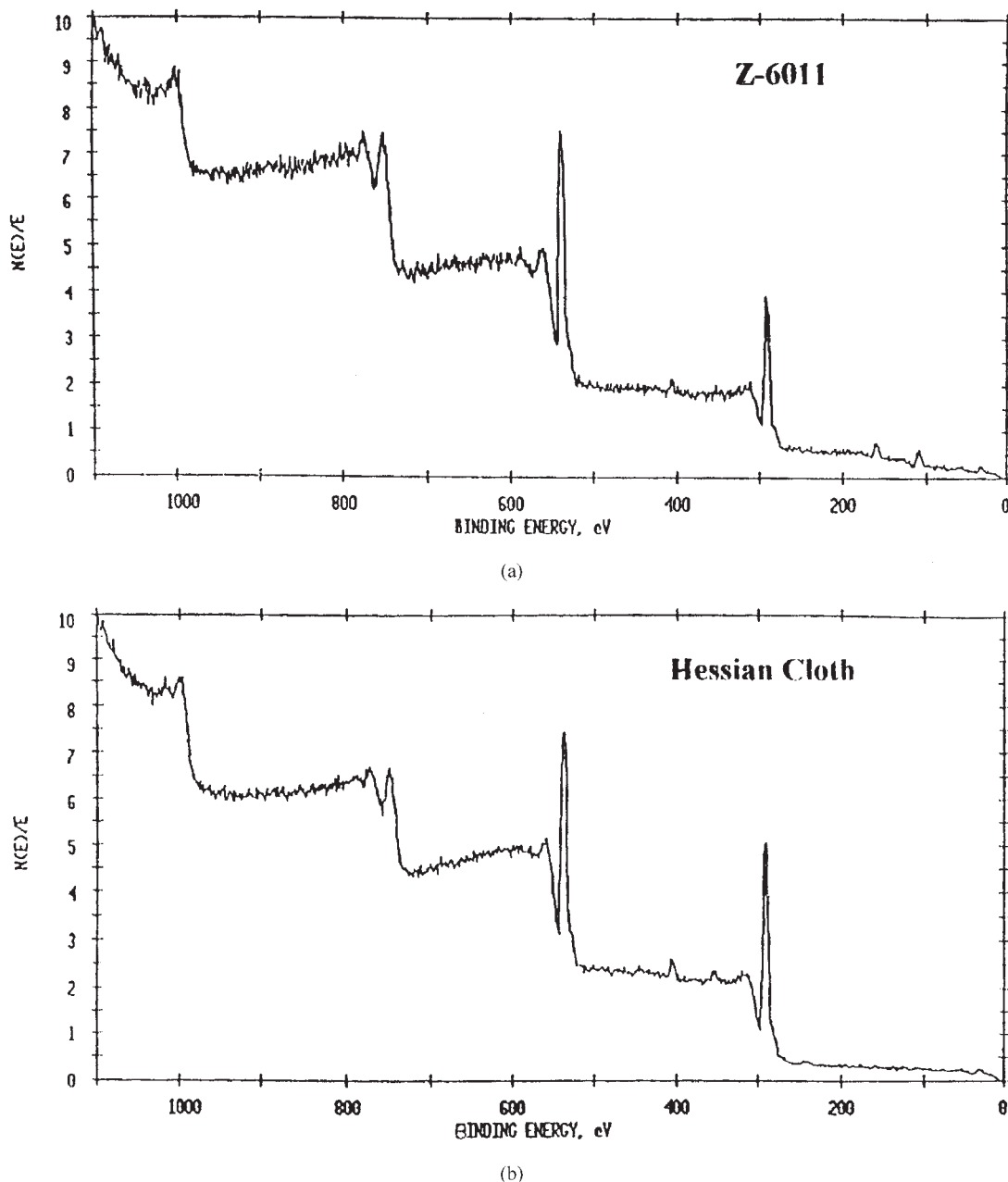

Scheme 1

Figure 2 XPS spectra of untreated (a) treated with Z-6011 (b) jute fiber.

four layers of PC film, using a Carver laboratory press (model 2518) at 5 ton pressure and 200°C temperature. The pressing phenomenon was continued up to 5 min. The jute content in the composite was about 32%.

X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) spectra of untreated HC, silanized HC, original PC, and the composites of PC with HC were recorded with a physical electronic instrument (PHI 5400 ESCA). All spectral data were collected using a Mg anode operated at a power of 300 W with an analyzer pass-energy of 33 eV.

Fourier transform infrared spectroscopy

The untreated jute fabrics, silanized jute fabrics, original PC, and their composites were investigated by Fourier transform infrared spectroscopy (FTIR, PerkinElmer, model spectrum 2000), using a technique of attenuated total reflectance.

Environmental scanning electron microscopy

The composite samples were fractured in a two-point bending mode and the fractured specimens were examined by an environmental scanning electron microscope (ESEM, model 2020, Electro Scan of Boston, MA).
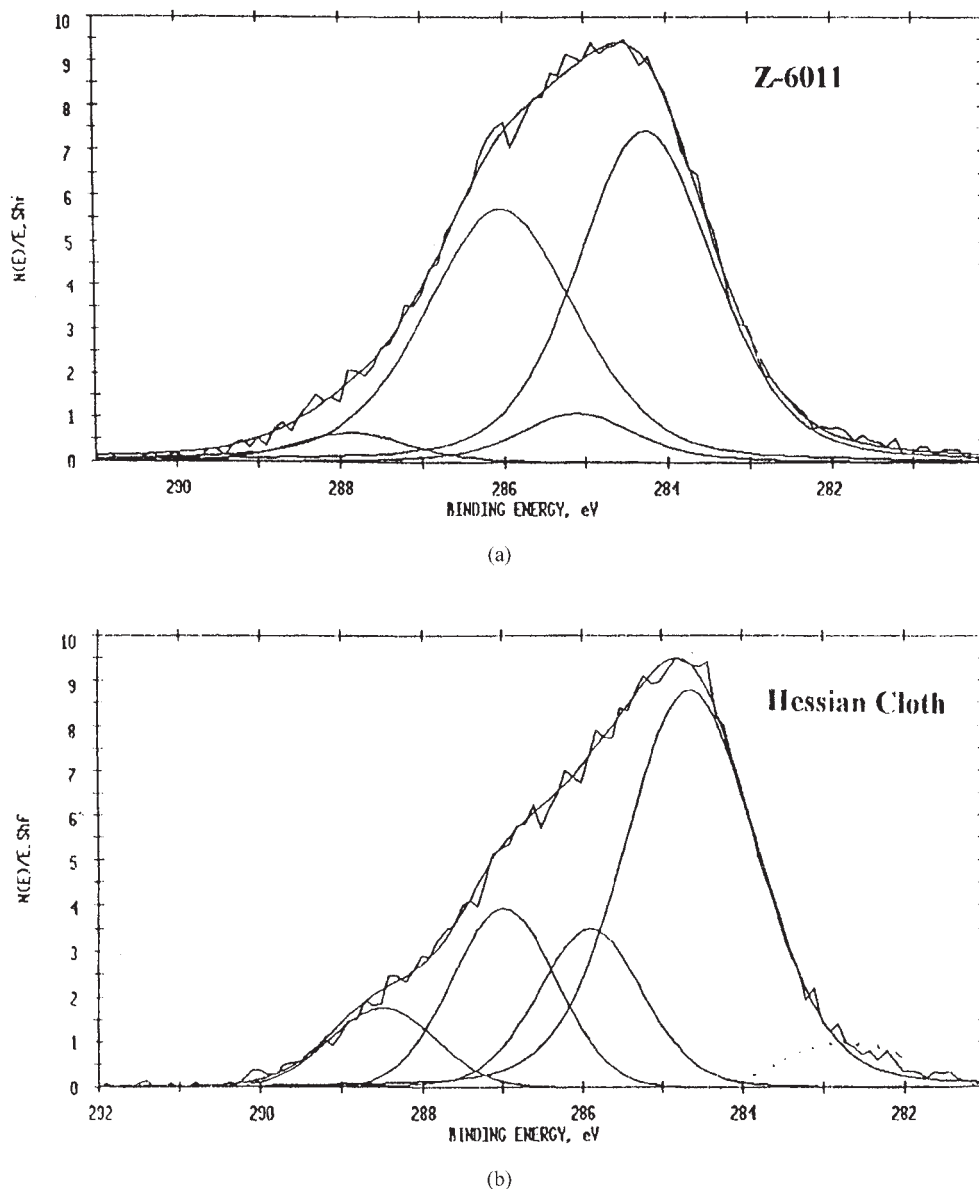
(a)

(b)

Figure 3 Carbon peaks of untreated (a) treated (b) jute fiber.

Differential scanning calorimetry

Thermal properties of the untreated and silanized jute samples were investigated using a DSC-50 apparatus of Shimadzu, Japan. The samples were inserted in the sample pan and sealed. Thereafter, they were introduced into the heating cell of the DSC to continuous heating upto 500°C at 10°C/min.

Dynamic mechanical analysis

Dynamic mechanical properties of the composites were measured as a function of temperature ranging from 30 to 180°C, using a dynamic mechanical analyzer (DMA-2980, TA Instruments). The heating rate was 3°C/min in multifrequency mode at an operating frequency of 1.0 Hz and an oscillation amplitude of 100 μm.

Mechanical tests

The tensile properties such as tensile strength and bending strength of untreated and treated composites were determined by means of a testing machine (IN-STRON, model-1011, UK) at a crosshead speed of 2 mm/min. All the results were taken as the average values of five samples.

RESULTS AND DISCUSSION

Characterization by FTIR

Both untreated and silanized jute samples were characterized by FTIR to confirm the chemical reaction between silanes and the cellulose backbone of the jute fiber. The spectra as depicted by the absorbance ver-
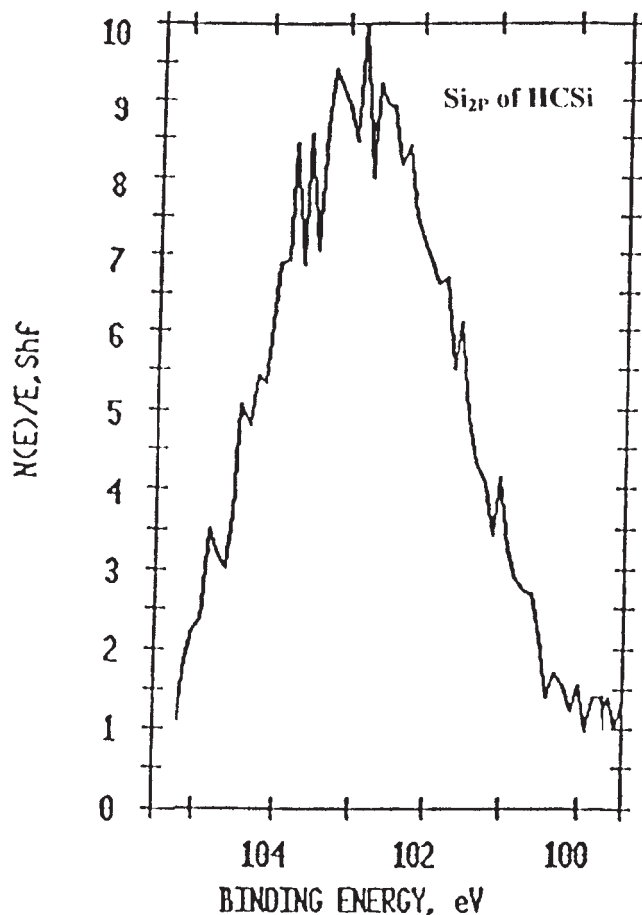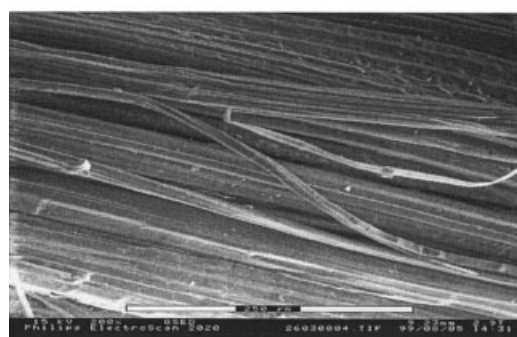
Figure 4 Si$_{2p}$ peak of Z-6011 treated jute fiber.

Untreated jute

(a)

Silanized jute

(b)

Figure 5 ESEM photographs of untreated (a) and Z-6011 (b) treated jute fiber.

Evaluation by XPS

X-ray photoelectron spectra of the electronic intensity versus bonding energy for the untreated and all silanized jute fibers were investigated and are shown in
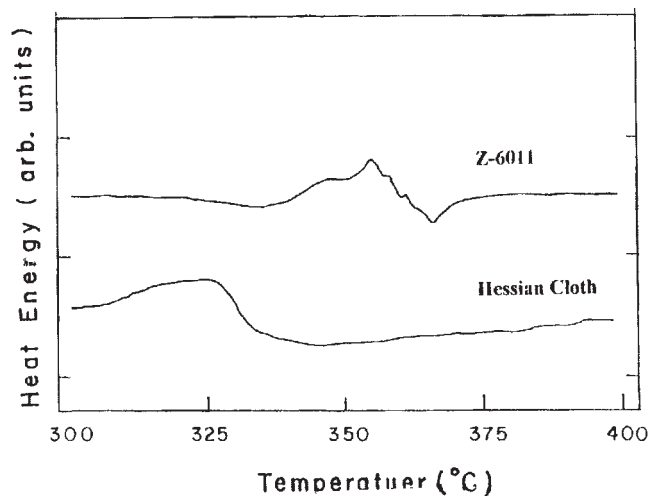
sus the wave number are taken in the range from 4000 to 700 cm^{-1} [Fig. 1(a)], but are shown from the region of 1700–700 cm^{-1} [Fig. 1(b)] to highlight the peaks. All silanized jute fabrics reveal absorption peaks at around 766 cm^{-1} (Fig. 1) which could be attributed to Si—C stretching bond.[7] A weak peak found at 847 cm^{-1} corresponds to a Si—C bond[8] and a broad peak that appeared in the range of 925–1105 cm^{-1} could be due to the presence of asymmetric stretching of Si—O—Si or Si—O—C (1014–1090 cm^{-1}) bond.[7,8] Such an absorption band for Si—O—Si is an indication of the existence of polysilonxanes deposited on the jute fibers but the band for Si—O—C assures a condensation reaction between the cellulose of the fibers and silane. A distinguished absorption peak is also observed at around 1200 cm^{-1} that corresponds to the Si—O—C bond.[7] New absorption bands are found at 1278, 1635, 1648, and 1715 cm^{-1} in Z-6011 treated fibers. The band at 1278 cm^{-1} is possibly from the C—N stretching of amines, while that at 1635 and 1715 cm^{-1} may be due to the NH$_2$ deformation.[9] Again, there are very weak peaks found at 860 and 980 cm^{-1}, which could be assigned to Si—OH. This confirms the fact that OH group of silanol reacts with cellulose or undergoes condensation reaction (Scheme 1).

Figure 6 DSC curves of untreated and silanized jute fiber.
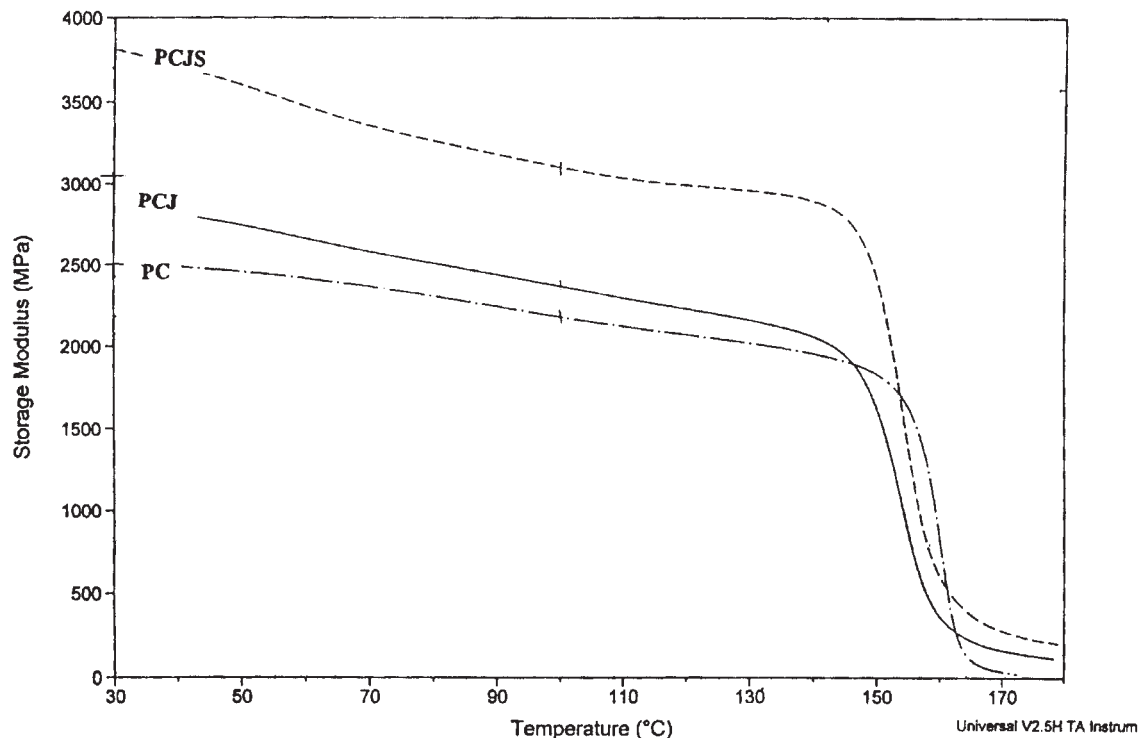
Figure 7 Storage modulus of PC and its composites of untreated (PCJ) and Z-6011 treated (PCS) jute.

Figure 2(a) and in Figure 2(b) for untreated HC and Z-6011 treated jute, respectively. Two distinct peaks of O_{IS} and C_{IS} are observed at 533 and 285 eV, respectively.[10,11] All the silanized jute fibers show characteristic emission peaks at energies ranging from 150 to 155 eV for 2s electron of Si (Si_{2S}) and 99–140 eV for 2p electron of Si (Si_{2P}). The carbon peaks of the aforementioned two samples are focused and then manipulated by a curve fitting program as shown in Figure 3. Four peaks of HC [Fig. 3(a)] are found at 288.48, 288.97, 285.88, and 284.62 eV for O=C=O, C—O or O—C—O or C—OH, C—O—O, and C—C (aliphatic) or C—H groups, respectively.[11] The presence of various types

of carbon peaks indicates that there are different types of compounds having different carbon linkage in the jute surface.[12–14] Surface treatment of the jute fiber with silane coupling agents is clearly obvious from the modified carbon peaks [Fig. 3(b)] of the corresponding groups that appear in Figure 3(a). The peak at 286.03 eV for C—O—Si or C—OH is intense and broad compared to that at 286–97 eV for C—OH group of untreated jute. Similar changes or variations in the shape of other peaks are also evident. Figure 4 represents the characteristic emission peak for silanized jute and indicates that a pair of peaks related to 2p electrons is found at approximately 102 eV as well as closer to 104 eV. The appearance of emission peaks at binding energy greater than 102 eV reflects the bonding of silicon atom with more than two atoms.[11–14] These findings of XPS demonstrate the presence of silicon atom in the jute fiber.
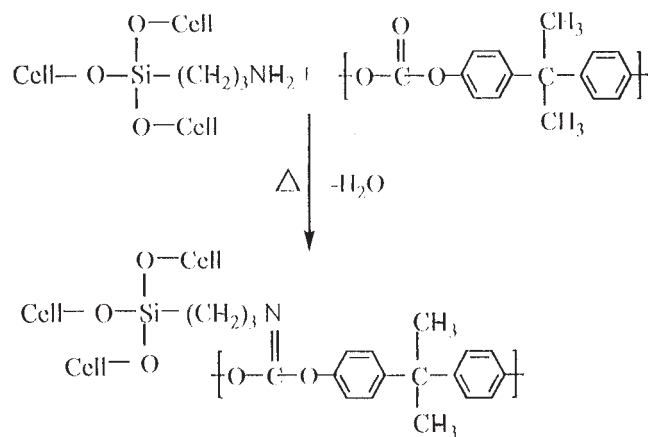
Surface topography by ESEM

The morphology of fiber surface or the surface topography was monitored by ESEM. ESEM photographs are presented in Figure 5, which shows that the surface of the untreated fiber is quite smooth [Fig. 5(a)], although the surface reveals many fragments due to silane treatment. The significant change in the topography is vigorous etching in the structure of the fiber surface treated by Z-6011 [Fig. 5(b)]. It is also observed
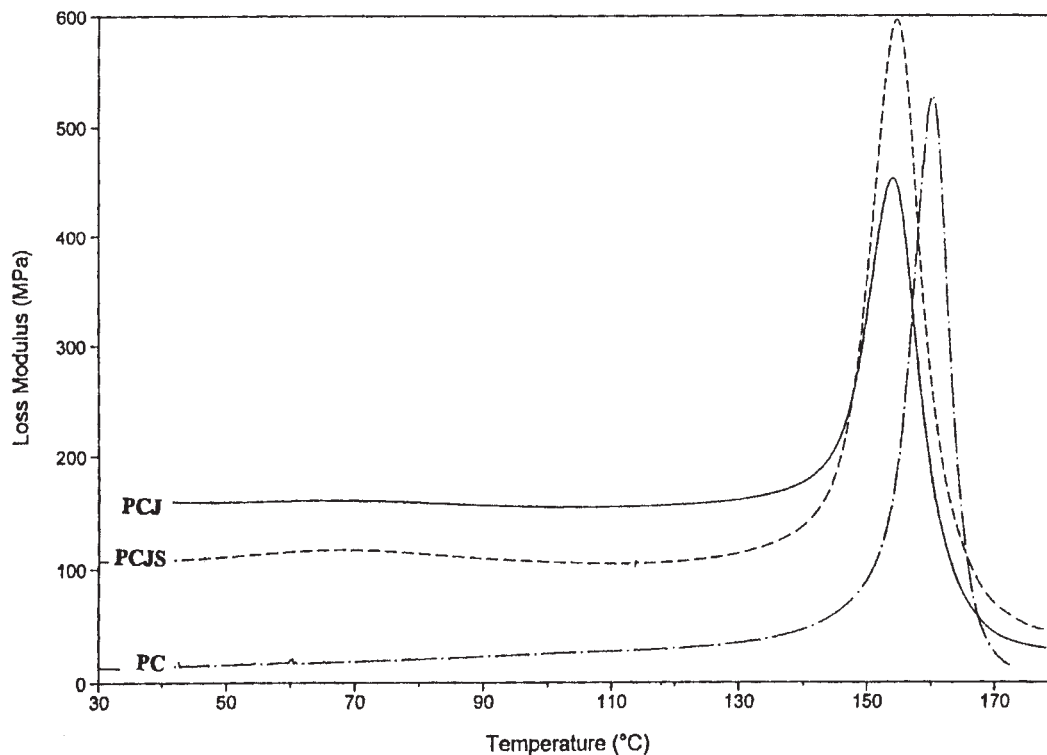

Scheme 2

Figure 8 Loss modulus of PC and its composites of untreated (PCJ) and Z-6011 treated (PCS) jute.

that there are many shallow and discontinuous grooves along the axial direction of the treated fiber.

Thermal analysis by DSC

DSC thermogrames obtained from both the untreated and silanized samples exhibit exothermic transitions as shown in Figure 6, where the peak temperatures appear differently with respect to simple conditions. The exothermic transition or melting temperature of untreated sample is 324°C, while that of Z-6011 is shifted to higher temperatures at 352°C. So, silanized jute samples are thermally stable than that of untreated jute.

Observation of PC-jute composites by dma

The E', E'', and tan δ for PC and its composites with untreated (PCJ) and treated (PCS) jute fabric were measured as a function of temperature. The E' is the property used to assess the total load bearing capacity of the materials investigated having the values shown in Figure 7. The initial storage modulus of the silanized jute composite was found to be increased, comparing both PC and untreated jute composite. The silanized jute composite reduces its moisture regaining capacity, whereas the untreated jute induces poor weather absorbability and adhesion charactersistics. The presence of moisture in the jute–PC interface pro-

motes the function of void due to the hydrophilic nature of jute and subsequently weakens the adhesion producing the composites with lower strength and stiffness. A much enhanced storage modulus of the composites is obtained in treated jute. The NH_2 group may undergo reaction with PC during composite fabrication as given in Scheme 2.

Figure 8 shows the values of E'' of the same kind of composites and PC as a function of temperature and exhibits that the loss modulus of PC is lower than that of its composites. Silanized jute composites produce higher values of loss modulus than untreated jute composites. This proves that the interfacial adhesion between PC and silanized jute fiber is higher than that of untreated jute. The tan δ value of PC shown in Figure 9 is greater than that of composites. It is clear that Z-6011 shows the lowest tan δ value. The damping property as obvious from tan δ values is an indication of all kinds of molecular movements existing in the materials. In a composite, molecular motion at the interface contributes to damping of the material. Strong interaction of fibers and matrix tends to reduce the mobility of the molecular chain at the interface and hence reduces the damping or tan δ values.[15]

Mechanical properties

The tensile strength (TS), bending strength (BS), bending E-modulus (BM), and tensile modulus (TM) were
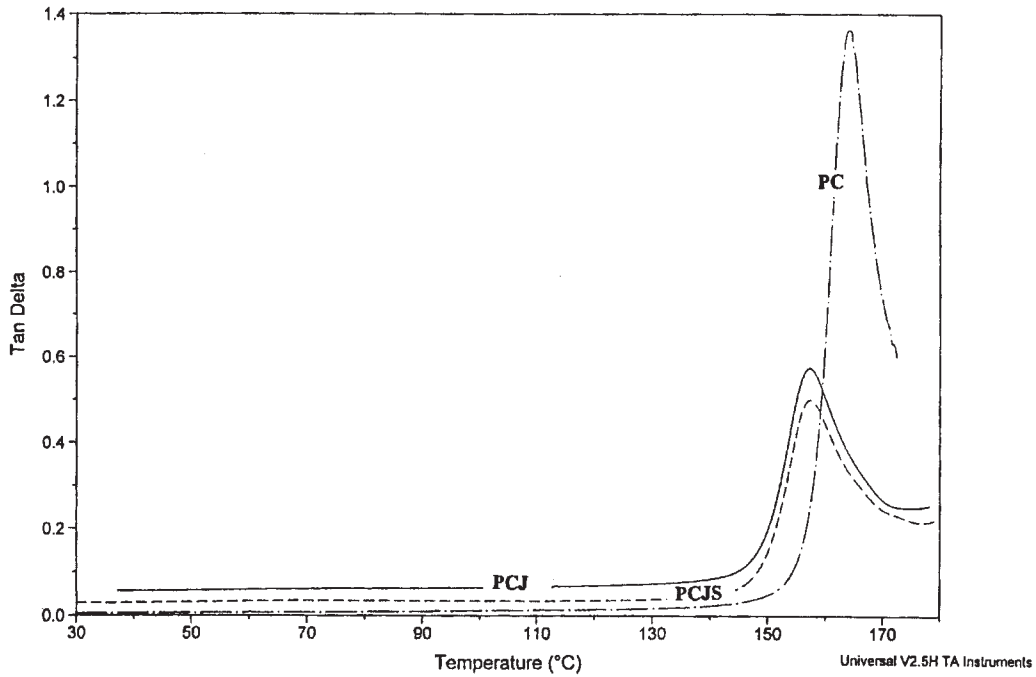
Figure 9 Tan δ of PC and its composites of untreated (PCJ) and Z-6011 treated (PCS) jute.

investigated to observe the reinforcement effect of the original and silanized jute fabrics. The relative change of mechanical properties in the composites prepared with treated fibers with respect to the untreated fiber is shown in Figure 10, and has been expressed by factors such as tensile strength factor (Tf), bending strength factor (Bf), bending modulus factor (BMf) and tensile modulus factor (TMf). The factors are derived from the ratio of the mechanical property of

composite to the corresponding property of untreated jute. The determination of such a factor like Tf is obtained by dividing the value of tensile strength of silanized jute composite (TSS) with the value of tensile strength of untreated jute composite (TSU) i.e., Tf = TSS/TSU; similarly, Bf = BSS/BSU, BMf = BMS/BMU and TMf = TMS/TMU. If the mechanical property of original jute fiber composite is considered to be unity, then a comparison of the results between Z-6011 and the original sample indicates 28, 35, 62, and 70% enhancement of the TS, BS, BM and TM, respectively.
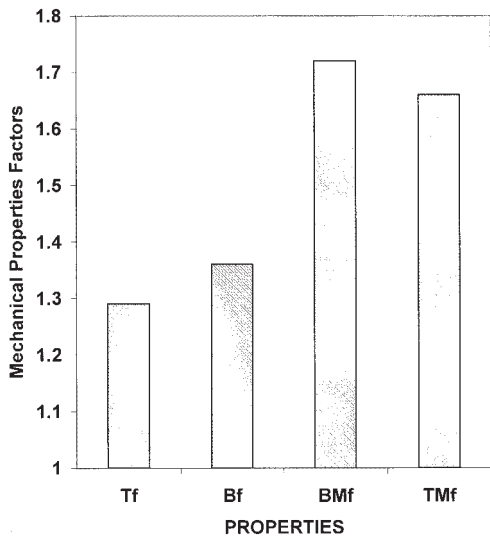

Figure 10 Mechanical properties' factors like Tf (tensile strength factor), Bf (bending strength factor), BMf (bending E-modulus factor) and TMf (tensile modulus factor) of the composites.
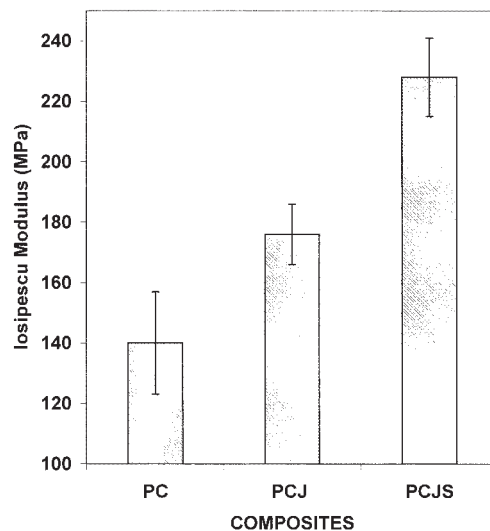

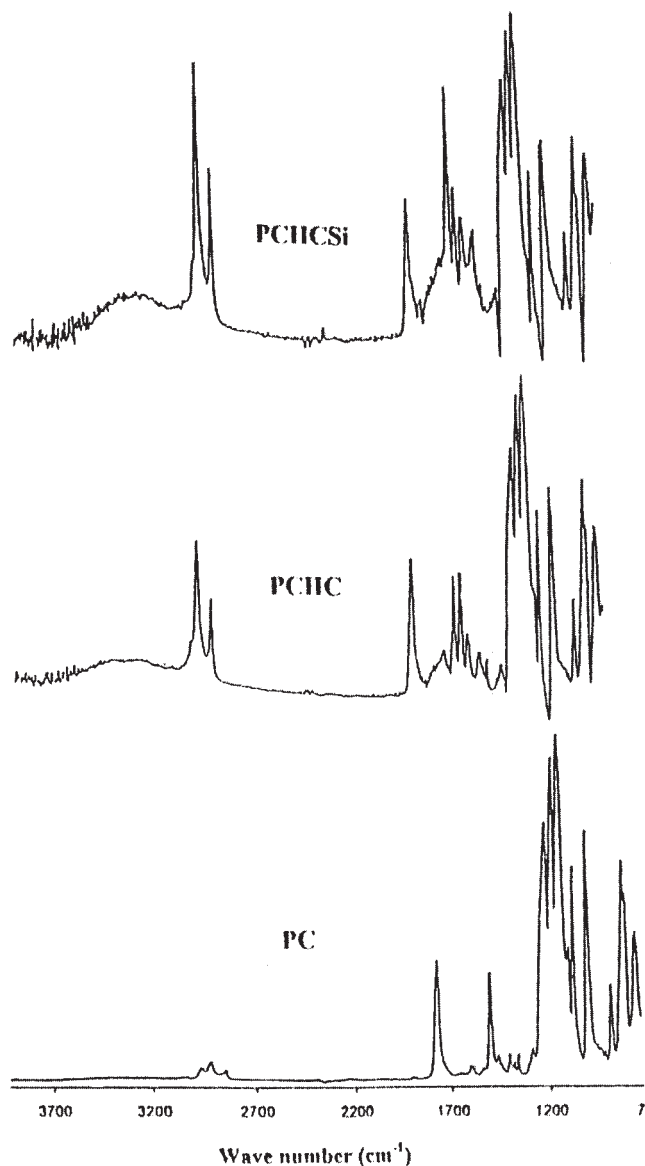**Figure 11** Iosipescu shear modulus of PC and its composites of untreated (PCHC) and Z-6011 treated jute.

Figure 12 FTIR spectra from 4000 to 700 cm^{-1} of PC and its composites of untreated (PCHC) and Z-6011 treated (PCH-CSi) jute.

In fact, Z-6011 consists of amino silanes having NH_2 group that may react with —[O—CO—O—] group of PC through condensation polymerization (reaction Scheme 2). The superior values of TS and BS for treated samples may be attributed to the fact that the silane treatment improves the interfacial bonding through the reactive groups thereby producing a rough surface topography.

Iosipescu shear test

Iosipescu shear test was performed with V-notched types of PC, PCHC, and PCHCSi samples. The samples were clamped between the gauges and kept in a

taut state. The shear stress was calculated by dividing the applied load with crosssectional area of the specimen. Each result was drawn along with standard deviation. Figure 11 shows the shear modulus of virgin PC and its composites of untreated jute (PCHC) and silanized jute (PCHCSi). Among the composites, Z-6011 treated jute composite registered the highest shear modulus, which is 64% and 28% higher than that of pure PC and untreated jute composite, respectively.

Characterization of PC-jute composite by IR

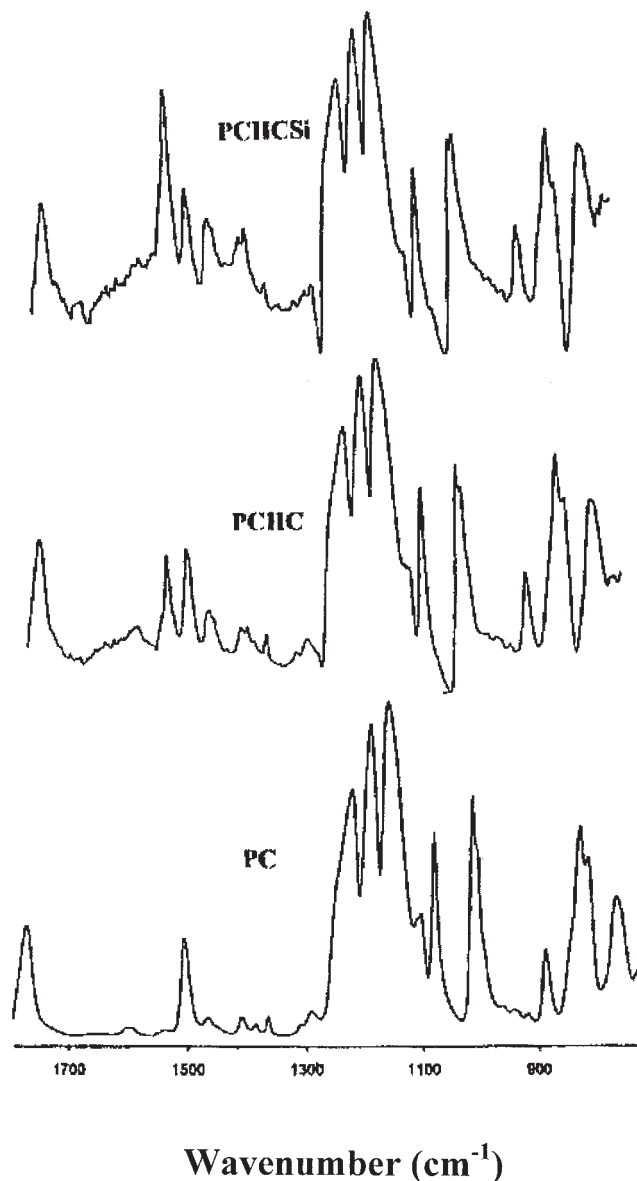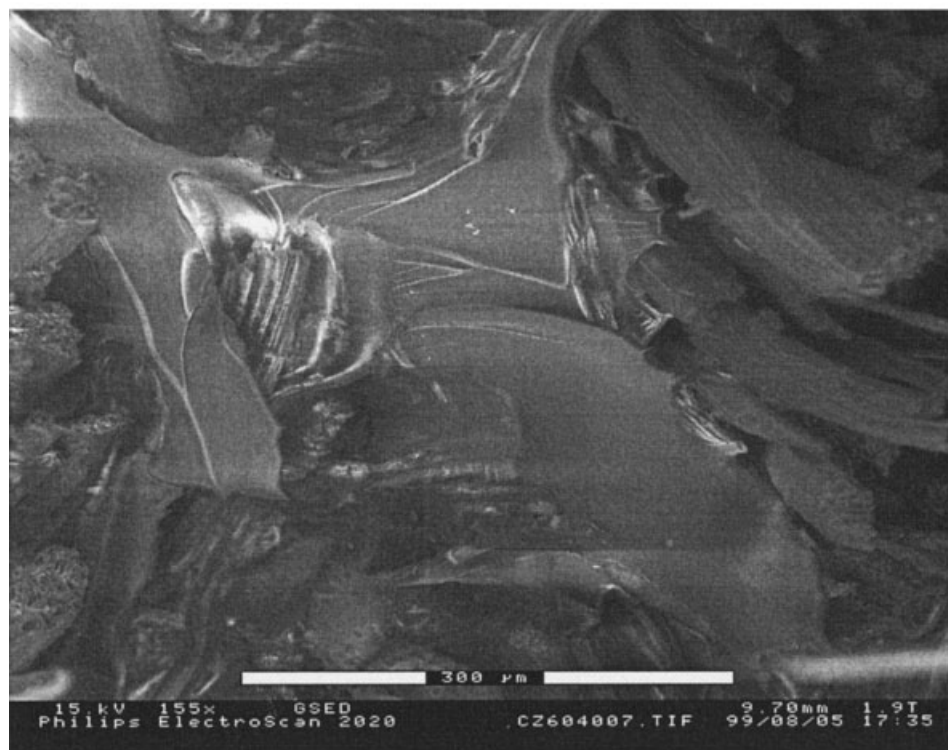The role of coupling agents was investigated by FTIR to understand the performance of untreated and

Wavenumber (cm^{-1})

Figure 13 FTIR spectra from 1800 to 700 cm^{-1} of PC and its composites of untreated (PCHC) and Z-6011 treated (PCH-CSi) jute.

(a)

Untreated Jute Composite

(b)

Silanized Jute Composite

Figure 14 ESEM photographs of fracture surfaces of untreated (a) and Z-6011 treated (b) jute composites.
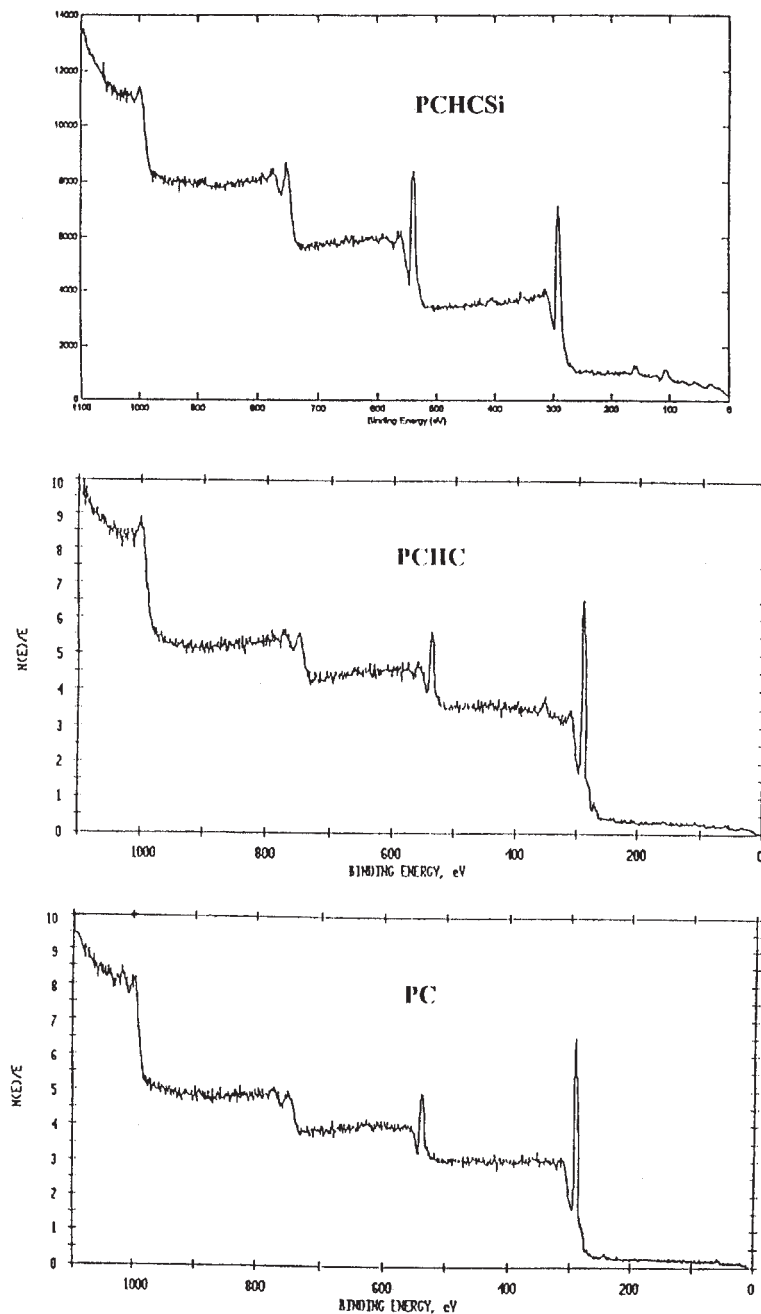
Figure 15 XPS spectra of PC and its composites of untreated (PCHC) and Z-6011 treated (PCHCSi) jute.

treated PCHC composites but the effect of Z-6011 has been presented here. Figure 12 (4000–700 cm^{-1}) and Figure 13 (1800–700 cm^{-1}) represent the IR spectra of PC, PCHC composite, and composites with silanized jute (PCHCS). The spectra of treated composites indicate new bond formation between HC and PC through coupling agent. The absorption bands are observed at 1568 and 1288 cm^{-1}, which are the characteristic bands of —NH deformation and C—N stretching mode, respectively.[9,16] A weak absorption band appeared at 1630 cm^{-1} specifies the C=N bond for imi-

nes like compound. For urethanes, the carbamate bands which are the combination of ester and amide appear in a position between that of the normal ester and amide. Thus, the results of IR spectra reveal that the primary amine (—NH$_2$) group of Z-6011 treated fiber combines with PC through the chemical reaction. There are a new band around 965 cm^{-1} arising possibly from the Si—C—O bond and other bands at 1004 and 1105 cm^{-1} corresponding to Si—O—Si. To distinguish all peaks in the composite of silanaized jute is very difficult because of the weak absorbance.

Interfacial properties

Interfacial properties of the composites both PCJ and PCJS were studied by ESEM. ESEM micrograph of the fracture surface of the composites are shown in Figure 14. A better dispersion of the fibers in the matrix is observed in the PCHCS composite. Chemical modification of the fibers prevents hydrogen bonds from being formed and causes the properties of the fiber surface and matrix.

Characterization of PC–jute composite by XPS

The chemical environment in PC and the composites of treated and untreated PC–jute were analyzed by XPS and the spectra obtained are shown in Figures 15. PC shows the characteristic peaks of carbon and oxygen (Fig. 13). PCHCSi shows characteristic emission peaks at the region of 99–140 eV for Si_{2P} (Fig. 15) and 150–155 eV for Si_{2S} (Fig. 15). One of the peaks at approximately 102 eV and the other closer to 104 eV (Fig. 16) are related to the 2p electrons. The N_{IS} peaks of HCSi [Fig. 17(a)] and PCHCSi [Fig. 17(b)] could be assigned to the presence of the amine group in the
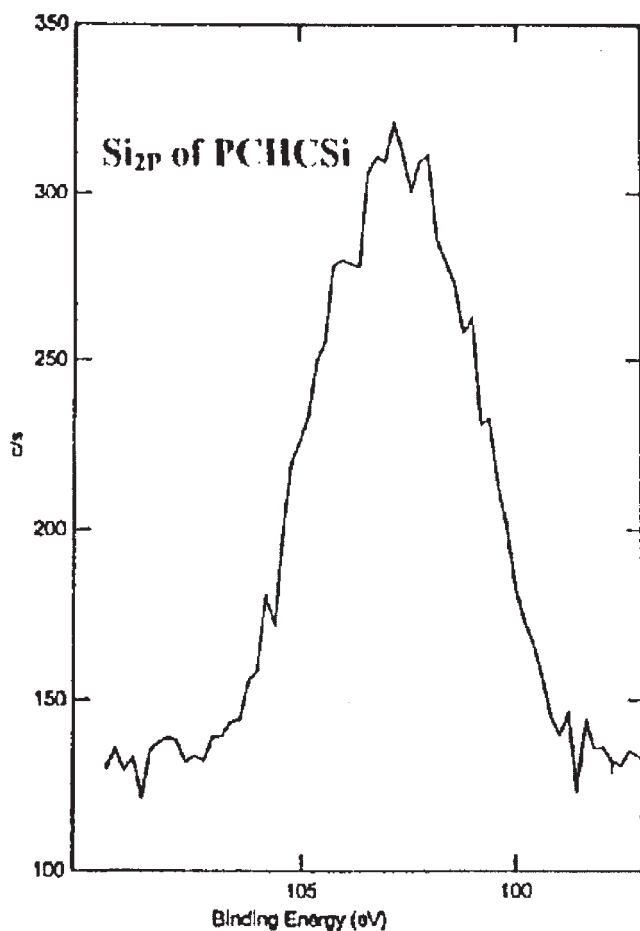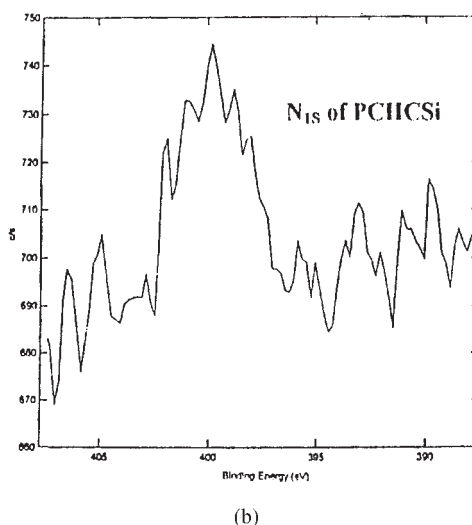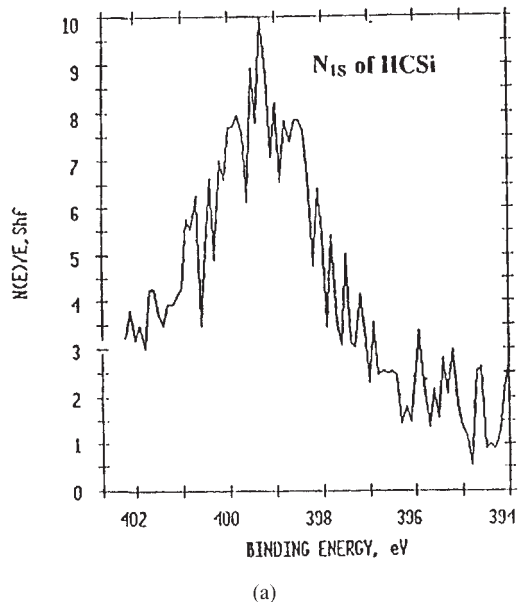

(a)

(b)

Figure 17 N_{Is} peak of Z-6011 treated jute fiber (a) and Z-6011 treated jute fiber composite (b).

coupling agent (Z-6011). The N_{IS} peak of the composite as shown in Figure 17(b) is shifted towards higher energies because of the formation of the tertiary amine group.[17]

CONCLUSIONS

Amino-silane coupling agent modified the jute–PC composite to improve the interfacial adhesion between jute fiber and PC. The analyses discussed earlier corroborate that γ-aminopropyl trimethoxy silane (Z-6011) is able to exhibit super performance for jute–PC composites. These investigations bear significant information for diverse applications of jute–PC composites.

Figure 16 Si_{2P} peak of PCHCSi composite.

References

1. Burger, H.; Koine, A.; Maron, R.; Mieck, K. P. Int Polym Sci Technol 1995, 22, 25.

2. O'Dell, J. L. In Proceedings of the 4th International Conference on Wood fiber-Plastic Composites, Madison, WI, May 12–14, 1997; p 280.

3. Oksman, K.; Sandlund, E. In Proceedings of the 2nd International Symposium on Natural Polymer and Composites—IS-NaPol/98, Sao Paulo, Brazil, May 10–13, 1998; p 79.

4. Mohanty, A. K.; Khan, M. A.; Sahoo, S.; Hinrichsen, G. J Mater Sci 2000, 35, 2589.

5. Isayama, K.; Hatano, I. (to Kanegafushi Kagaku Kog) U.S. Pat. 3,971,751 (1976).

6. Brod, G. L.; Conte, L. B., Jr. (to Union Carb. Corp.) U.S. Pat. 3,632,557 (1972).

7. Ishida, H.; Koeing, J. In Proceedings of the 31st Annual Technical Conference, Reinforced Plastic/Composites Institute, The Society of Plastic Industry: Washington, DC, 1976; Section 6-C, p 17.

8. Briteher, L.; Kehoe, D.; Matisons, J.; Swincer, G. J. Macromolecules 1995, 28, 3110.

9. Pouchert, C. J., (Ed.) The Aldrich Library of Infrared Spectra, 3rd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1988; pp 62, 123, 1535.

10. Wagner, C. D.; Riggs, W. M.; Muilenberg, G. E., (Ed.). Hand Book of X-ray Photoelectron Spectroscopy; Perkin Elmer Corp.: MN, 1979.

11. Toth, A.; Blazso, I.; Banhegyi, M. G.; Bognerp, A. J Appl Polym Sci 1994, 52, 1239.

12. Morra, M.; Ochicllo, E.; Garbassi, F. J Appl Polym Sci 1993, 48, 1331.

13. Hassan, M. M.; Islam M. R.; Khan, M. A. J Adhes Sci Technol 2003, 17, 623.

14. Khan, M. A.; Hassan, M. M.; Drzal, L. T. Compos A 2004, 36, 71.

15. Hua, L.; Zadorecki, P.; Flodin, P. Polym Compos 1987, 8, 199.

16. Plueddemann, E. P. Silane Coupling Agents; Plenum: New York, 1982; p 103.

17. Everhart, D. S.; Reilley, C. N. Anal Chem 1981, 53, 665.