Viscose Fiber/Polyamide 12 Composites: Novel Gas-Phase Method for the Modification of Cellulose Fibers with an Aminosilane Coupling Agent

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ABSTRACT: The objective of this study was to improve the adhesion between viscose fibers and polyamide 12 and, thereby, the mechanical properties of the corresponding composites. The cellulose fiber surface was chemically modified in the vapor phase with a silyl coupling agent, aminosilane [(3-aminopropyl) triethoxysilane]. This new gas-phase treatment for cellulose fibers proved to be highly effective. Relative to composites without the coupling-agent treatment, the tensile strength of the composites (40/60 wt % fiber/polymer) increased from 49.3 to 87.4 MPa; the improved adhesion between the fibers and matrix induced by the coupling agent was observed under a scanning electron microscope. The presence and bonding of the coupling agent on the fibers after the reaction was confirmed by solid-state ^{29}Si-NMR. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4478–4483, 2006

Key words: adhesion; compatibilization; electron microscopy; extrusion; fibers

INTRODUCTION

Thermoplastics reinforced with cellulose fibers are reasonable alternatives for thermoplastic/glass-fiber composites. The main advantages of cellulose fibers over traditional glass fibers are their low density, reduced tool wear, and biodegradability. Wood and natural fibers also have drawbacks, in particular, a limited processing temperature ($< 200°C$) due to thermal degradation of the fiber and poor compatibility between the hydrophilic fiber and the hydrophobic matrix.[1,2]

Because of the low thermal stability of the fiber, the most commonly used thermoplastics in cellulose composites are polypropylene, polyethylene, and polystyrene. Polyamides (PAs) have also been tested as matrices for wood-fiber composites.[3,4] However, the processing temperature is too high for most PAs. PA 12 is the most suitable matrix for wood/plastic composites because of its relatively low melting point (180°C). It also has a low moisture absorption compared other PAs.

A common method for improving the adhesion between the polymer and fiber and, hence, the mechanical properties of a composite is the use of a coupling agent. Alkoxysilanes were tested as coupling agents in glass-fiber composites in the late 1940s, and the first commercial silane-based coupling agents for this purpose, vinyltriethoxysilane and (3-aminopropyl)-triethoxysilane, were introduced in the 1960s.[5] Alkoxysilanes have also been applied in wood fiber/thermoplastic composites. At present, however, the most common coupling agent for these composites are maleated polyolefin and isocyanate-grafted polyolefin coupling agents.

In previous studies, our focus has been on polypropylene/viscose-fiber composites.[6,7] PA is less commonly included in wood-fiber composites. In this study, we examined the mechanical properties of PA 12/viscose-fiber composites. Because little information is available on the effect of coupling agents in PA/wood-fiber composites, another objective of the study was to examine the effect of an aminosilane coupling agent on the mechanical properties of the composites. During this study, it become clear that the method of treatment with the coupling agent was critical for the achievement of good mechanical properties. Different processes for the treatment of fibers with the coupling agent were therefore compared.

EXPERIMENTAL

Materials

The fiber was bright viscose (6 mm in length, supplied by Säteri Oy, Valkeakoski, Finland). The thermoplastic was Grilamid L 16 natural (PA 12 grade, manufactured by EMS-Grivory, Gross-Umstadt, Germany). (3-Aminopropyl) triethoxysilane (99%), dicumyl peroxide (98%), toluene, and methanol (analytical grade) were from Sigma-Aldrich (Schnelldorf, Germany). Toluene

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(dried with 4-Å molecular sieves) was distilled over sodium and benzophenone under a nitrogen atmosphere. Methanol was distilled before use. Ethanol (99.5 wt %, Altia, Rajamäki, Finland) was used as obtained. The chemicals used in the ninhydrin dye test were ethyl acetate (99.9%, Fluka, Schnelldorf, Germany), ninhydrin (Merck p.a, Espoo, Finland), acetic acid (100%, Merck), and heptane (99%, Lab Scan Analytical Sciences, Hasselt, Belgium).

Pretreatment of the viscose fibers with the coupling agent

In all, 16 series were prepared, 14 of which contained aminosilane. The series are described in Table I. Series 1 was the PA 12 reference, whereas series 2 represented a composite without the coupling agent. Series 3–16 were prepared to study the effect of the coupling agent on the mechanical properties of the composites. The effects of different coupling-agent treatments and the moisture content of the fibers were tested.

The fibers were treated with aminosilane in methanol solution according to the literature[8] (series 6, Table I). The viscose fibers were dried in an oven (80°C) for 6 h, and the dried fibers (15 g) were then placed in a glass reactor containing 8.4 g of dicumyl peroxide dissolved in 500 mL of distilled methanol (the dicumyl peroxide content in the final methanol solution was 2 wt %). A nitrogen atmosphere was applied in the reactor. Aminosilane was added (17.8 mL; the final aminosilane content in the methanol solution was 4 wt %), and the reaction mixture was refluxed for 3 h (60°C). The mixture was continuously stirred during the reaction. Then, the reaction the fibers were washed with methanol and oven-dried for 20 h (60°C).

In series 3–16, the fibers were treated with aminosilane in the gas phase (Fig. 1). Series 3–5 were used to clarify the influence of the reaction time on the gas-phase reaction. In these studies, fibers (30 g) were dried in the oven for 6 h (80°C). For the 3-h reaction, 20 mL of aminosilane was added to the bottom of the desiccator. For longer reaction times (6 or 18 h), the amount of aminosilane was increased to 30 mL. Dried fibers were placed on a perforated porcelain plate above the aminosilane (Fig. 1). The desiccator was closed and evacuated. Once a vacuum was achieved (< 10 mbar), the valve of the reaction chamber was closed, and the temperature of the oil bath was raised to 110°C. Timing commenced when a temperature of 110°C was achieved. After the reaction, the fibers were washed with distilled toluene and dried in the oven for 20 h (60°C). Treated fibers were stored in the desiccator for further study.

In series 8–16, the fibers were dried in the oven for 1 h (100°C), and the dry weight was measured (gravimetric method). Dried fibers were then rinsed with ion-exchanged water and dried in the oven (60–110°C) until the moisture content of the fibers had reached the predetermined value (between 11.1 and 37.7 wt %). The next step was the aminosilane gas-phase treatment (18 h). After the reaction, the fibers were washed with distilled toluene and dried in the oven overnight at 60°C.

TABLE I
Description of the Series of PA/Viscose Fiber (40/60 wt %) Composites

Series	Treatment method	Time (h)	Moisture content of the fibers (wt %)	Tensile strength/ standard deviation (MPa)
1	None[a]	—	—	40.0 ± 1.4
2	None	—	—	49.3 ± 0.7
3	Gas phase	3	—[b]	75.8 ± 3.5
4	Gas phase	6	—[b]	76.9 ± 2.1
5	Gas phase	18	—[b]	79.7 ± 1.0
6	Liquid phase	3	—	60.6 ± 1.5
7	Gas phase	18	5.9[c]	79.3 ± 1.3
8	Gas phase	18	11.1	85.8 ± 0.9
9	Gas phase	18	15.0	86.4 ± 1.3
10	Gas phase	18	22.7	84.2 ± 0.9
11	Gas phase	18	28.6	87.4 ± 1.6
12	Gas phase	18	34.4	77.2 ± 1.8
13	Gas phase	18	34.4[d]	67.7 ± 3.0
14	Gas phase	18	34.4[e]	72.3 ± 2.7
15	Gas phase	18	34.4[d,e]	68.7 ± 4.2
16	Gas phase	18	37.7	78.3 ± 3.6

[a] PA 12 reference.
[b] Oven-dried.
[c] Stored under an atmospheric moisture
[d] Fibers extracted after the treatment.
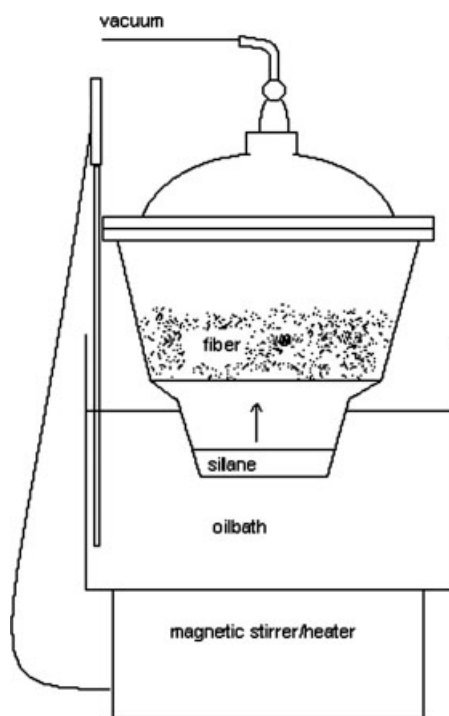[e] Fibers cured after the treatment.

Figure 1 Experimental setup used for the gas-phase treatment of the fibers.

Four series (12–15) were prepared to study the effect of the curing and extraction of the fibers after the gas-phase reaction (series 12–15). In the first stage, 60.5 g of fiber (moisture content of the fibers = 34.4 wt %) was treated in the gas phase for 18 h. The batch was then divided into two parts. One part was cured for 2 h at 110°C *in vacuo* (< 5 mbar in series 14–15), whereas the other was dried for 20 h at 60°C (series 12–13). To determine whether physically sorbed aminosilane was present in the fibers, an ethanol extraction was carried out series 13 and 15.

Mechanical testing

Mechanical tests were carried out with material testing equipment (Zwick Z010/TH2A model 2001, Ulm, Germany). Calculations were done with TestXpert version 8.1 software. The crosshead speed was 50 mm/min. At least five standard tensile specimens were tested for each series. Specimens were stored at ambient temperature (22–23°C) and in ambient humidity for 2 days before testing. The tensile strengths of the materials were obtained by the determination of the maximum force that the material withstood divided by the cross-section of the specimen.

Scanning electron microscopy (SEM)

The fracture surfaces of the composites were studied with a LEO 1550 scanning electron microscope (Darmstad, Germany) operated at 5 kV. The surfaces of the samples were coated with gold before the measurements.

Solid-state NMR

The ^{29}Si-NMR cross-polarization/magic-angle spinning (CP–MAS) experiment was carried out with a Bruker AMX-400 spectrometer (Karlsruhe, Germany). Operating frequencies were 400.13 MHz for proton and 79.49 MHz for silicon. A 7-mm ZrO_2 rotor was used as a sample holder. The ^{29}Si-NMR CP–MAS spectra were acquired with a 90° pulse, a 5-ms contact time, a 6-s recycle delay, 15,000 scans, and 4.5-kHz magic-angle spinning.

Elemental analysis

The nitrogen content of aminosilane-modified fibers was determined with a CE Instrument EA 1110 elemental analyzer (Milan, Italy). The temperature of the oven was 1010°C.

Ninhydrin dye test

Ninhydrin was used to confirm the presence of amines in the aminosilane-treated fibers (series 13). The ninhydrin solution was prepared by the dissolution of 5 g of ninhydrin in a solution of ethanol (75 mL), ethyl acetate (25 mL), and acetic acid (3 mL) and the addition of heptane (1 mL).

For the dye test, a few drops of the solution were placed on the fibers so that they were soaked with the solution. For reference, untreated viscose fibers without any treatment were treated with the same solution. When the dyed fibers from series 13 were dried, a violet blue color appeared, which confirmed the presence of primary amines; no color formation was observed for the reference.

Extrusion and injection-molding of PA/viscose-fiber composites

Fibers (40 wt %) treated with the coupling agent and PA 12 (60 wt %) were mixed with a DSM twin-screw midi-extruder (at a temperature of 200°C for 4 min) (Heerlen, Holland). After the mixing, the composite material was pelletized and extruded once again (200°C for 3 min). From the extruder, the composite material was directly fed with a separate feeding cylinder into the DSM microinjection molding device to produce tensile test specimens (cylinder temperature = 215°C, mold temperature = 150°C, air pressure = 9 bar in injection). PA 12 reference specimens were manufactured with the following parameters: extrusion temperature = 200°C for 4 min, temperature of the cylinder = 200°C, temperature of the mold = 60°C, and injection pressure = 5 bar. The width and thickness of

the tensile specimen were 5.0 and 1.5 mm, respectively, with a gauge length of 35 mm.

RESULTS AND DISCUSSION

Effect of aminosilane treatment on the tensile strength of the composites

The tensile strength of PA 12 and PA 12/viscose-fiber composites were determined for reference. The test results are reported in Table I. The tensile strength of the PA 12 was 40 MPa (series 1). Reinforcement of PA12 with cellulose fiber (40 wt %) increased the tensile strength by 23% up to 49.3 MPa (series 2). The increase in strength was probably due to the hydrogen bonding between the cellulosic fiber and the PA matrix.

In series 6, fibers were treated with aminosilane in methanol solution according to ref. 8. The strength of the solution-treated composites was 23% better than that of composites without the coupling agent (series 6 vs series 2). The improved strength in series 6 could be explained by enhanced hydrogen bonding promoted by aminosilane.

When the fibers were treated with aminosilane in the gas phase for 3 h, the strength of the composites increased by 54% (75.8 MPa) compared with the composite without fiber pretreatment (series 3 vs series 2). Relative to the fibers treated with aminosilane in methanol solution, the strength of the composites was 25% greater (series 3 vs series 6). The increase in strength in series 3 might have been due in part to the hydrogen bonding between free amine groups of the covalently (silyl ether bond/bonds) bonded aminosilane and carbonyl oxygen of PA 12.

Increasing the gas-phase reaction time from 3 to 18 h (series 5) improved the strength of the composites as well. However, the increase was modest (from 75.8 to 79.7 MPa).

Increase in the moisture content of the fibers before gas-phase treatment

In series 3–5, the fibers were oven-dried before the gas-phase treatment, but in series 7–16, the composites were manufactured from fibers with different moisture contents. The tensile strength of the composite that contained 5.9 wt % moisture (stored under atmospheric moisture) in the fibers before the gas-phase reaction was almost equal to the strength of the composite with dried fibers (series 7 vs series 5). However, when the moisture content of the fibers was increased to 11.1 wt %, the strength improved 8.3% (series 8 vs series 5). The tensile strength of the composites in series 9–11, where the moisture content was increased up to 28.6 wt %, was in the range 84–87 MPa and remained relatively constant. However, with a further increase in the

moisture content (to 34.3 wt %), the strength decreased by 13% (series 11 vs series 12). Figure 2 illustrates the effect of the initial moisture content of the fibers on the strength of the composites.

Series 7–16 show how the moisture content of the fibers before the gas-phase reaction influenced the aminosilane/cellulose reaction and that addition of excessive water led to reduced strength in the composites. These results might be explained in terms of the reaction of alkoxysilanes. Alkoxysilanes react with water to form silanols.[9] A silanol is in reactive form; it can interact with the hydroxyl groups of cellulose. More water on the fiber surface means more reactive silanols, which up to a certain point, leads to better binding between the cellulose and aminosilane. The decrease in strength of the composites with an excessive amount of water might be due to the formation of a weak boundary layer.[5] A weak boundary layer is the result of the self-condensation of aminosilanes rather than a reaction with the cellulose.

Curing and extraction studies

The aim in this study of series 12–15 was to examine how the curing (2 h at 110°C) of the aminosilane on the cellulose surface after the gas-phase reaction affected the function of the coupling agent. The fibers were treated with aminosilane in the gas-phase reactor for 18 h, and the moisture content of the fibers was 34.4 wt %. The fibers were extracted with ethanol (series 13 and 15) to clarify the nature of the bonding between fiber and aminosilane. A similar extraction and curing study was published for silanes applied onto cellulose fibers in water solutions.[10]

Curing (2 h at 110°C *in vacuo*.) of the aminosilane-treated fibers after the reaction led to a slightly lower tensile strength in the composites. The strength of the composites was 7% less than that of composites with no curing after the gas-phase reaction (series 14 vs series 12).
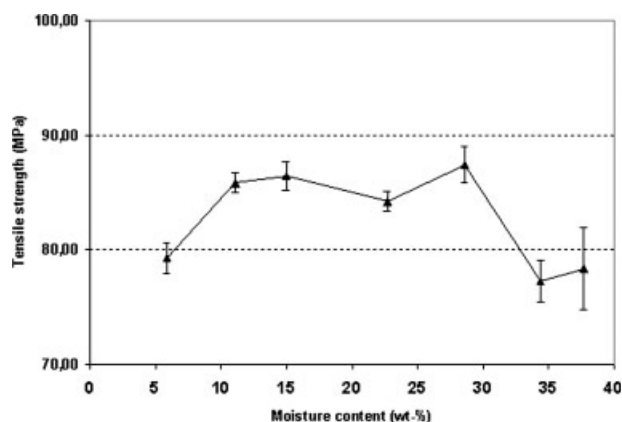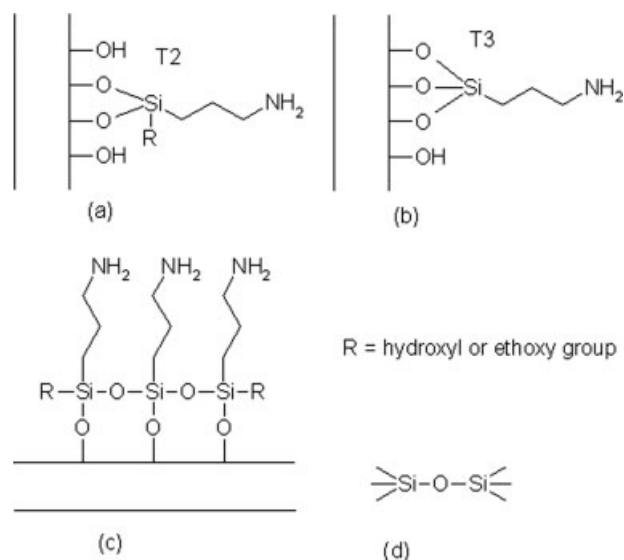

Figure 2 Effect of the moisture content of the fibers before gas-phase treatment on the tensile strength of the composites.

After the extraction of the fibers with ethanol for 15 h, the strength of the composites decreased, regardless of whether the fibers were cured or not. The strength of the composites decreased by 14% when fibers were merely extracted after the reaction (series 13 vs series 12) and by 12% when fibers were cured and then extracted (series 15 vs series 12). The decrease in strength with the extraction of the composites indicated that the fibers contained a small amount of noncovalently bonded aminosilane, which detached from the surface during extraction, but even this aminosilane increased the strength of the composites.

Studies of aminosilane attachment on the fiber surface

According to the elemental analysis results, the nitrogen content of fibers in series 3–16, in which the aminosilane coupling was used, varied between 0.04 and 0.75 wt %, which corresponded to hydrolyzed aminosilane contents of 0.4–7.5 wt %. The bonding mode of aminosilane to the cellulose was studied by solid-state ^{29}Si-NMR. The ^{29}Si CP–MAS spectrum of the fibers from series 11 showed resonances at −60.5 ppm (T2, two ethoxy groups of the silane have reacted either with the cellulose or with another silane) and −68.2 ppm (T3, three ethoxy groups of the silane have reacted either with the cellulose or with another silane). According to the literature, in the case of silanes on silica (SiO$_2$) surfaces,[11–13] a chemical shift of −60.5 ppm corresponds to a structure where two ethoxy/silanol groups have reacted with the silica surface and

Figure 3 Fracture surface of tensile specimen of series 2.

two siloxane bridges have formed. The chemical shift of −68.2 ppm corresponds to a silicon nucleus with three siloxane bridges.

NMR data for series 11 showed that two or three ethoxy groups of aminosilane reacted. Under the conditions we used, the silanol groups of aminosilane could have reacted with hydroxyl groups in the cellulose or/with another silanol (Scheme 1), whereas the amino groups stayed unreacted.[10] The ninhydride test confirmed that the amino end of aminosilane remained unreacted. Moreover, the high strength of the aminosilane-treated composites suggested covalent bonding between the aminosilane and cellulose.

SEM analysis of the fractured composite surfaces

After the tensile tests, SEM images were taken of the fracture surface of the tensile specimens of series 2, 5, and 9. The images revealed that in composites without the aminosilane coupling agent (Fig. 3, series 2), the fibers were pulled out from the matrix, which was clear evidence for poor adhesion between the fiber and the

Scheme 1 Proposed chemical structures on the fiber surface that correlated with the observed NMR resonances: (a) aminosilane reacted onto cellulose with two silylether bonds, (b) aminosilane reacted onto cellulose with three silylether bonds, (c) aminosilane reacted onto cellulose but also condensed with another aminosilane, and (d) aminosilane polymerized.
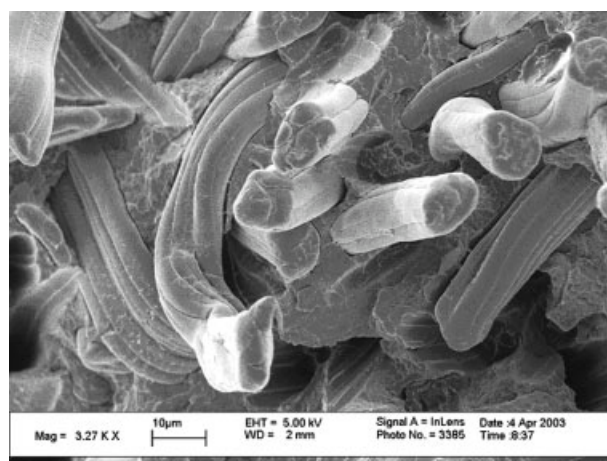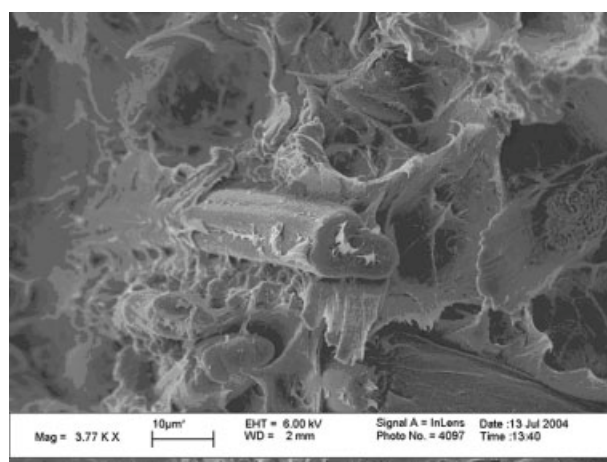
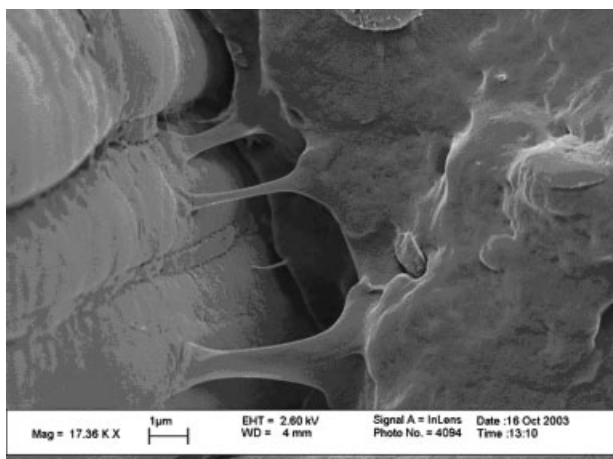**Figure 4** Fracture surface of tensile specimen of series 9.

Figure 5 Fracture surface of tensile specimen of series 5.

matrix. When fibers were treated with aminosilane in the gas phase, the fiber pullouts were mostly prevented, which was an indication of improved adhesion between the fiber and the matrix (Fig. 4, series 9). A close up of the fiber/matrix interface (Fig. 5, series 5) revealed strings of plastic material attached on the fiber surface. We concluded that the SEM images clearly supported binding of the PA12 matrix and the fiber together.

CONCLUSIONS

According to mechanical tests, aminosilane is a highly effective coupling agent in viscose fiber/PA 12 composites. Relative to composites without fiber treatment, the strength of the composites increased as much as 95% with the best coupling-agent treatment. The gas-phase treatment, where the alkoxysilane was applied on the cellulosic fibers with heat *in vacuo*, proved to be effective. The gas-phase treatment was a simple solvent-free and catalyst-free method for treating fibers with a volatile coupling agent.

The strength of the composites subjected to the gas-phase treatment was observed to depend on the mois-

ture content of the fibers. When the moisture content was optimized to 28.6 wt %, the tensile strength was 87.4 MPa, which was the highest value obtained. A further increase in moisture content decreased the strength of the composites.

NMR studies revealed that the interaction between aminosilane and fibers was based on the formation of two or three adjacent silyl ether bonds. The high mechanical strengths of the aminosilane-containing composites also indicated an enhanced interaction between PA and the fibers. SEM images of the fracture surfaces of the composites showed that fiber pullout in composites where the aminosilane coupling agent was applied was prevented; this supported improved adhesion between the fibers and the matrix.

References

1. Mohanthy, A. K.; Mishra, M.; Hinrichsen, G. Macromol Mater Eng 2000, 276/277, 1.
2. Blendzki, A. K.; Reihmane, S.; Gassan, J. Polym Plast Technol Eng 1998, 37, 451.
3. Jacobson, R.; Caulfield, D.; Sears, K.; Underwood, J. In Proceedings of the Sixth International Conference on Woodfiber–Plastic Composites; Forest Product Society: Madison, WI, 2001; p 127.
4. Jacobson, R.; Caulfield, D.; Sears, K.; Underwood, J. In Proceedings of the Sixth International Conference on Woodfiber–Plastic Composites; Forest Product Society: Madison, WI, 2001; p 27.
5. Mittal, K. L. Silanes and Other Coupling Agents; VSP BV: The Netherlands, 1992; p 1.
6. Paunikallio, T.; Kasanen, J.; Suvanto, M.; Pakkanen, T. T. J Appl Polym Sci 2003, 87, 1895.
7. Paunikallio, T.; Suvanto, M.; Pakkanen, T. T. J Appl Polym Sci 2004, 91, 2676.
8. Coutinho, F. M. B.; Costa, T. H. S.; Carvalho, D. L. J Appl Polym Sci 1997, 65, 1228.
9. Olotnitzsky, M.; Steinmetz, J. R. J Vinyl Additive Technol 1995, 1, 109.
10. Gandini, A.; Abdelmouleh, M.; Boufi, S.; Salah, A. B.; Belgacem, M. N. Langmuir 2002, 18, 3203.
11. Ek, S.; Iiskola, E. I.; Niinistö, L.; Pakkanen, T. T.; Root, A. Chem Commun 2003, 2032.
12. Cardiano, P.; Sergi, S.; Lazzari, M.; Piraino, P. Polymer 2002, 43, 6635.
13. Buszewski, B.; Jezierska, M.; Ostrowska-Gumkowska, B. Mater Chem Phys 2001, 72, 30.