Influence of Functionalized Silanes on Mechanical Properties of Wood Sawdust Reinforced ABS Composites

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Abstract

This research is to demonstrate that wood-plastic composites can be formulated using acrylonitrile butadiene styrene (ABS) as the matrix polymer. This was accomplished by compounding the polymer with wood sawdust particles 10 phr. Three different silane coupling agents e.g. aminopropyltrimethoxysilane, 3glycidoxypropyltrimethoxysilane and vinyltrimethoxysilane treated on the wood sawdust surface and each was compounded with ABS using a twin-screw extruder. Addition wood sawdust tended to increase the modulus of the composites, while their strength was reduced. The extent of tensile property improvement depended on the chemical nature of the silane coupling agent employed. The effects of chemical treatments with different silanes were investigated by Fourier transform infrared spectroscopy, scanning electron microscopy and mechanical testing. The results illustrated that aminopropyltrimethoxysilane was the most likely coupling agent for improving Young's modulus and tensile strength of the wood sawdust/ABS composites. While vinyltrimethoxysilane was the most efficient agent to outperform the elongation at break of the wood sawdust/ABS composites.

Introduction

Recently, natural-fiber-reinforced polymers have attracted the attention of researchers because of their advantages over established materials. Plant fibers are naturally available and biodegradable which caused lesser ecological impact than mineral fillers. Natural fibers also contributed to their low cost, low-density, lower abrasive nature, higher specific strength, and higher modulus of elasticity [1,2]. Despite the mentioned above advantages, it is difficult to achieve strong

interfacial adhesion between the hydrophilic surface of the wood and the hydrophobic thermoplastic polymers [3]. Because wood plastic composites (WPCs) are true hybrid materials, they have strength and stiffness properties that are somewhere between wood and plastic [2,3]. The mechanical properties of reinforced polymers can be improved by optimizing the interphase between the matrix and the filler by coupling agents [1, 4-7] and also the properties of the filler, by taking into consideration the amount used in the blend. To improve adhesion between matrix and filler, the surface of material can be modified by chemical treatments or by use of coupling agents.

ABS is a thermoplastic that combines advantages in performance between commodity and engineering thermoplastics. Its use as matrix in WPCs could lead to composites with properties superior to those made with common commodity plastics.

The main purpose of this study is to investigate the effect of different coupling agents on the tensile properties of wood sawdust-reinforced composites. In order to increase the adhesion between these two dissimilar materials, it is logical to use a third material containing special functional groups which can adhere to both surfaces. Among all kinds of coupling agents, organofunctional silanes have been chosen because of commercial availability and the results they could offer.

Experimental

Materials

ABS (GA300 by IRPC, Thailand) was chosen as matrix of the composite. The melt flow rate was 30 g /10 min. Wood sawdust particles obtained from carpentry and wood working processes and supplied by V.P. Wood Co., Ltd. (Bangkok Thailand). The average size of sawdust particles used in this work was in the range of 100-300 μ m. The wood sawdust content of the composites was 10 parts per hundred (phr) of ABS was used to investigate the effect of coupling agent addition. Three kinds of silane coupling agents were used in this study, 3-glycidoxypropyltrimethoxysilane supplied by Shin Etsu Chemical Co., Ltd. (Thailand). Vinyltrimethoxysilane and aminopropyltrimethoxysilane produced by Sigma-Aldrich, Inc., Germany. The chemical structures and descriptions of these agents are listed in Table 1.

Chemical descriptions	Chemical Structures
3-Glycidoxypropyltrimethoxysilane	осн ₂ о-сн ₂ о-сн ₃ осн ₃
Aminopropyltrimethoxysilane	OCH ₃ H ₂ N(CH ₂) ₃
Vinyltrimethoxysilane	осн ₃ H ₂ C === сн == si == осн ₃ осн ₃

Table 1. The chemical structures and descriptions of silane coupling agents.

With these coupling agents, the influence of the chemical structure of the silane coupling agents on the interfacial strength of the ABS/wood sawdust composites could be examined. The silane concentration was varied as 0.5, 1.0, 1.5 and 2.0% by weight of wood.

Method

Wood treatment and compounding

ABS pellets were dried in oven at 82°C for 6 h to get rid of the probable negative effect of humidity on processing. Silane coupling agents are diluted with deionized water to a concentration of approximately 0.5 to 2.0%. With silane coupling agents that have low solubility in water, a combination of 1.0% of acetic acid in deionized water is recommended for this work. Acetic acid is used to increase the hydrolysis rate and improve the stability of the silanols. After the coupling agent has been added and stirred continuously for 30 minutes. The hydrolysis of the silane would be completed when the solution had become nearly transparent.

The silane solutions were sprayed into wood sawdust in a high speed mixer at 25 Hz for 5 min. The treated surface of wood was oven-dried at 110° C until the weight constant. The treated wood was mixed by dry-blending with ABS plastic in a high speed mixer at 25 Hz for 3 min. The components were homogenized in corotating twin screw extruder at 190° C at 100 rpm. An injection molding machine, Battenfeld Corp. (A 250 CDC), was used to prepare the specimens for mechanical tests.

Characterization and testing

The modified wood sawdust was examined using Fourier transform infrared spectroscopy (FTIR, Nicolet impact 410). A universal testing machine (LLOYD Instruments Corp. LR 50K) was used for tensile properties measurements, according to BS 2782: Part 3 (1996) Methods 320A with a crosshead speed of 50 mm/min.

Results and Discussion

The effects of coupling agents on the mechanical properties of WPCs have been investigated. Mechanical properties of neat ABS and untreated-wood sawdust/ABS composite at wood content 10 phr were shown in Table 2. There was no significant difference found in the Young's modulus of the untreated wood sawdust/ABS composites as 1.44 ± 0.04 GPa and the neat ABS as 1.40 ± 0.04 GPa. This might be because the untreated wood sawdust had no adhesion bonding between the filler and polymer matrix.

Sample	Young's Modulus	Tensile	% Elongation
	(GPa)	Strength (MPa)	at Break
Neat ABS	1.40 ± 0.04	42.23 ± 0.58	21.06 ± 0.23
Wood/ABS	1.44 ± 0.03	36.21 ± 0.32	4.229 ± 0.63

Table 2. Tensile properties of neat ABS and untreated-wood/ABS composite

When each of silanized agents was introduced into the wood/ABS composite to comparatively investigate its coupling effect. As illustrated in Figure 1, it showed the increase of Young's modulus for the treated wood/ABS composites result in improved the adhesion between wood sawdust and ABS matrix. Among three treated silanes, the Young's modulus of aminopropyltrimethoxysilane treated wood sawdust/ABS is the highest. Also, the Young's modulus of wood/ABS composites using glycidoxypropyltrimethoxysilane treated wood system is higher than vinyltrimethoxysilane treated wood/ABS composite. These can be explained by the presence of active amino groups helping the silane treatments to have other stronger covalent bonds with the ABS matrix. The covalent bond of (C-O) might take place between the oxirane ring of 3-glycidoxypropyltrimethoxysilane and (C \equiv N) of ABS which is supposedly stronger than covalent bond of C=C between vinyltrimethoxysilane and ABS.



Figure 1. Effect of silane coupling agent types and contents on Young's modulus of ABS/wood sawdust composites.



Figure 2. FTIR spectra of (a) neat ABS (b) untreated wood/ABS composite (c) ABS/wood-aminopropyltrimethoxysilane (d) ABS/wood-3glycidoxypropyltrimethoxysilane and (e) ABS/wood-vinyltrimethoxysilane

The probable interactions between the polymer chains and the organofunctional groups of three coupling agents are responsible for this study. Some interactions could be formed by the attractive forces between the dipoles and also by primary bonding. Covalent forces are definitely stronger than those forces between the dipoles. There is no question of aminopropyltrimethoxysilane having the biggest effect on the surface adhesion of polymer-filler. For both 3-glycidoxypropyltrimethoxysilane and vinyltrimethoxysilane as coupling agent, these silanes may form the dipole-dipole moments between C-O of 3-glycidoxypropyltrimethoxysilane and acrylonitrile. Also, for vinyltrimethoxysilane, the adhesion between C-C covalent bonds might be from either acrylonitrile or butadiene. To investigate the intensity of coupling effect, the mechanical properties of treated composites were thereby measured and compared with the untreated ones as discussed earlier.

A group of FTIR spectra as shown in Figure 2 showed the adhesion of chemical reactions from which modified wood surface interacted with the polymer could be verified by the FTIR spectra. For example, Figure 2a showed the FTIR peaks of neat ABS for $-C\equiv N$ groups at 2237.41 cm⁻¹. Whereas Figure 2c was for aminopropyltrimethoxysilane-treated wood sawdust/ABS composites which illustrated peaks for $-C\equiv N$ groups at 2239.55 cm⁻¹ and for -C=N groups at 1648 cm⁻¹. There was no new peak occurring in the 3-glycidoxypropyltrimethoxysilane-treated wood sawdust/ABS composites as depicted in Figure 2d. The $-C\equiv N$ peak was observed to slightly shift at the wave numbers from 2237.41 cm⁻¹ of neat ABS to 2238.21 cm⁻¹ of treated wood/ABS composites. For vinyltrimethoxysilane-treated sawdust/ABS composites as seen in Figure 2e showed peak of C=C of this silane which appeared at 1637.14 cm⁻¹. The occurrence of the -C=N, and C=C peak proved the covalent bonding as proposed in the Figure 2.

In addition, the optimum content of each silane coupling agents are also depicted in Figure 1. The optimum amount of either aminopropyltrimethoxysilane or 3-glycidoxypropyltrimethoxysilane for treated wood sawdust was at 0.5 %wt. Whilst the optimum amount of vinyltrimethoxysilane treated wood/ABS composite was at 1.5 %wt. of wood sawdust.

Self-condensation reaction that may occur onto the surface could possibly form flexible polysiloxane molecules on the surface. The surface reinforcing mechanism could be affected because as such flexible polysiloxane molecules would probably reduce the adhesion of the wood sawdust and the polymer matrices. These flexible polysiloxane molecules from self-condensation reaction might be one of the reasons for the decrement trend of the tensile modulus even with the increase of silane coupling agents as shown in Figure 1.



Figure 3. Effect of silane coupling agent types and contents on tensile strength of ABS/wood sawdust composites

Similar observation was found for the effect of silane coupling agent contents on tensile strength of the composites as shown in Figure 3. It can be seen that the tensile strength of composites decreased when compared to the neat ABS because of the poor compatibility between wood and ABS and also the inadequate distribution of wood sawdust in the matrix. The interactions of silanized wood sawdust and ABS were taken place but the amounts of silane coupling agent usage were limited.

The percentages of elongation at break significantly decreased from 21.06 for neat ABS to 4.23 for untreated wood sawdust/ABS composite as shown in Table 2. It was likely due to the wood fibers obstructing the chain mobility of polymer matrix. The effect of silane coupling agent types and contents on the elongation at break for treated wood sawdust/ABS composites were shown in Figure 4. With the incorporations of silane treated wood in ABS, the elongation at break slightly improved when compared to the one without silane treatment.



Figure 4. Effect of silane coupling agent types and contents on elongation at break of ABS/wood sawdust composites.

Addition of vinyltrimethoxysilane at 1.0%wt or higher of wood sawdust/ABS would show relatively higher percentages of the elongation at break than the others. This could be the effect of double bonds (C=C) in vinyltrimethoxysilane leading to the flexibility of this silane treated system. Thus, it showed the highest amount of elongation at break for all except at the low content as mentioned. Elongation at break of silanized-treated composites are higher than the untreated composites because of plasticity behavior of polysiloxane, therefore polymer chains could slip pass by each other more easily.

Summary

The effects of functionalized silane coupling agents on the mechanical properties of wood sawdust and ABS composites have been investigated. Three different silane coupling agents, aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and vinyltrimethoxysilane, were treated on the wood sawdust surface. The extents of mechanical properties improvement depended on the chemical nature of the silane coupling agent employed. With the limitation on the contents usage, aminopropyltrimethoxysilane was the most likely coupling agent for improving Young's modulus and tensile strength of the wood sawdust/ABS composites. Vinyltrimethoxysilane was the most efficient agent to increase the elongation at break of the wood sawdust/ABS composites.

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