

# Effects of Silane and MAPE Coupling Agents on the Properties and Interfacial Adhesion of Wood-Filled PVC/LDPE Blend

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**ABSTRACT:** Composite samples were prepared from Poly(vinyl chloride)/low-density polyethylene (PVC/LDPE) blend, compatibilized by PA20 (methyl methacrylate-*co*-butyl acrylate copolymer), and reinforced by different levels of rubber-wood sawdust. To improve the mechanical properties of the composites, Silane A-137 (Octyltriethoxy silane), Silane A-1100 ( $\gamma$ -aminopropyltriethoxy silane), or MAPE (maleic anhydride-grafted-polyethylene) were introduced. It was found that the additions of Silane A-137, Silane A-1100, and MAPE could improve tensile and impact properties of the composites, regardless of the sawdust contents. Physical or chemical interactions for all coupling agents with the wood-PVC/LDPE composites used were proposed in this work. Silane A-137 or MAPE tended to give better improvement in the mechanical

properties of the composites than Silane A-1100, because of the presence of the nonpolar chain ends of Silane A-137 or MAPE molecules. Besides, the addition of either Silane A-137 and MAPE or Silane A-1100 and MAPE at different ratios into the wood-PVC/LDPE composites was also studied. The experimental results suggested that the optimum mechanical properties could be obtained using Silane A-137 : MAPE of 1% : 2% wt sawdust. The morphological and thermal properties of the composites were also examined using SEM and DMA techniques, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3523–3530, 2008

**Key words:** polymer blend; poly(vinyl chloride); composite; wood sawdust; mechanical properties

## INTRODUCTION

Polymer blend and composites have been studied extensively, and their properties were dependent on miscibility and structure of all components.<sup>1</sup> Three or more phases in polymer blend and composite systems have increasingly attracted scientists, researchers and industries, especially, efforts to improve and modify the composite properties. Poly(vinyl chloride) (PVC) is one of the most widely used thermoplastics in packaging and construction applications. PVC products are likely to be contaminated by olefin polymers such as polyethylene (PE) and polypropyl-

ene (PP).<sup>2</sup> PVC/PE blend has been utilized in several applications such as, blister packing, electric cable sheathing, but its mechanical properties and service performance are much inferior because of their phase incompatibility. One of the most common methods to improve the mechanical properties of the incompatible blend is to introduce a suitable compatibilizer. Previous work<sup>2</sup> has shown that mechanical, morphological, and thermal properties of the PVC/LDPE blend were significantly improved by addition of poly(methyl methacrylate-*co*-butyl acrylate) (PA20).

In general, fiber reinforced polymer composites yield a unique combination of high performance, great versatility, and processing advantages at favorable cost savings. Among other fillers used for such polymeric products, wood fibers become an important class of the reinforcing materials because they show many advantages, including low density, little demand during processing, little requirement on processing equipment, biodegradability, high stiffness, and relatively low price.<sup>3</sup> However, the wood fibers are incompatible with the polymer because of their hydrophilic character that results in uneven dispersion in the composites, thus a poor stress transfer

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TABLE I  
Chemical Structures and Descriptions of Silane Coupling Agents

Silane types	Chemical description	Chemical structure
Silane A-137	Octyltriethoxy silane	$\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OCH}_2\text{CH}_3)_3$
Silane A-1100	$\gamma$ -aminopropyltriethoxy silane	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$

between the matrix and the filler and unsatisfactory properties of the final produced.<sup>3</sup> As a consequence, researches have been focused on improving interfacial adhesion of the fiber and polymer phases, usually through use of coupling agents, such as silane coupling agents<sup>4–10</sup> and maleic anhydride-grafted-polymer.<sup>5–8,10–17</sup> The interfacial adhesion can be both chemical and physical, which are referred to as covalent and hydrogen bonds, and molecular entanglements, respectively.

Our previous work<sup>2</sup> has shown that the compatibility between PVC and low-density polyethylene (LDPE) could be improved by incorporating poly(methyl-methacrylate-co-butyl acrylate) (PA20) which acted as phase compatibilizer, but the mechanical strength of PVC/LDPE blends decreased by the addition of wood fibers. The work was now extended to improve the interfacial adhesion between the wood fiber and PVC/LDPE blend by introducing different chemical coupling agents at various dosages, PA20 being used as the selected compatibilizer for PVC and LDPE phases.<sup>2</sup> The level of interfacial adhesion was evaluated through mechanical, morphological, and thermal properties of the wood filled PVC/LDPE composites. Possible molecular interactions among materials phases (PVC, LDPE, wood, PA20) in the composites were also proposed.

## EXPERIMENTAL

### Raw materials

1. Poly(vinyl chloride) (PVC, B0504BLA suspension grade, K value = 66) was supplied by Thai Plastics and Chemicals, Co. (Bangkok, Thailand). The compound composed of 1.2 phr calcium stearate, 1.2 phr tetrabasic lead sulfate, 0.1 phr PE wax, and 4 phr calcium carbonate.
2. Low-density polyethylene (LDPE, LD1905F) with MFI of 5 (tested at 21.6 N and 190°C) was obtained from Thai Polyethylene, Co. (Bangkok, Thailand).
3. The compatibilizer used was poly(methyl methacrylate-co-butyl acrylate) (PA20), supplied from Srithepthai Co. (Thailand). In this work, PA20 was used as the compatibilizer for PVC and LDPE phases.
4. Rubber-wood sawdust (*Hervea Brasiliensis*), collected from local furniture factory, was sieved

through standard sieve of 50–80 mesh, corresponding to the particle length of 180–300  $\mu\text{m}$ . The sieved sawdust was dried in an oven at 105°C for 2 h before use.

5. Octyltriethoxy (A-137) and  $\gamma$ -aminopropyltriethoxy (A-1100) silane coupling agents were supplied by Sigma-Aldrich, Co. (Bangkok, Thailand) and Optimal Tech, Co. (Bangkok, Thailand), respectively. The chemical structures of both silane coupling agents are given in Table I. Maleic anhydride-grafted-polyethylene (MAPE; Fusabond MB100D) with MFI of 2 g/10 min (tested at 21.6 N and 190°C) was supplied by Chemical Innovation, Co. (Bangkok, Thailand).

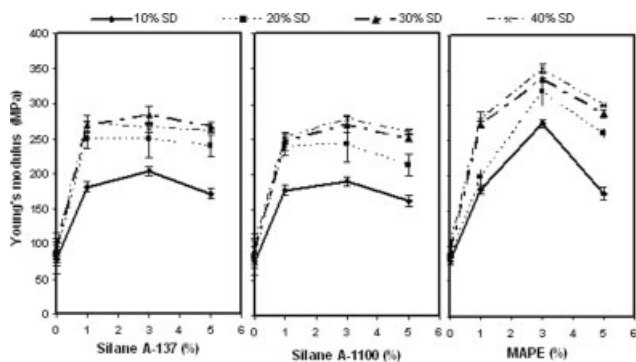
### Blend preparation and experimental design

Melt-blending of PVC with LDPE was performed using a single-screw extruder (Thermo Haake Poly Drive) with a screw speed of 60 rpm and a temperature range from 170 to 190°C, starting from feed zone to die zone. The obtained extrudates were further compounded in a two-roll mill (LabTech Engineering, LRM 110) for 10 min using the temperature of 165°C before transferring into a compression molding machine (LabTech Engineering, LP 20). The compressing temperature and time were set at 200°C and 8 min, respectively. Since this work aimed to study the effect of coupling agent type and content on the mechanical properties of the PVC/LDPE blend filled with various contents of wood sawdust, the three steps of experimental procedures were noted.

- First, the amount of the sawdust was varied at 10, 20, 30, and 40% to study the effect of sawdust content on the properties of the PVC/LDPE (100/40) blends using PA20 for 15% wt of LDPE.
- Second, Silane A-137, Silane A-1100, and MAPE at 1.0, 3.0, and 5.0% wt of wood sawdust were used to improve properties of the composites.
- Finally, the influence of using mixed coupling agents (Silane : MAPE) on interfacial strength was studied, the percentage ratios of Silane : MAPE used being 2 : 1, 1 : 1, and 1 : 2.

### Mechanical properties

All mechanical tests were carried out at the temperature of 23°C  $\pm$  1°C and relative humidity of 50%  $\pm$  5%. It should be noted that the mechanical property

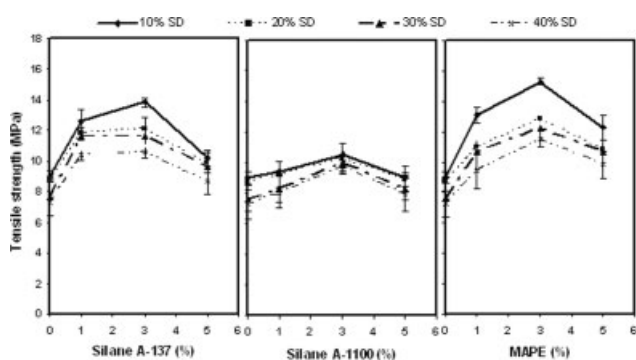


**Figure 1** Young's modulus of the sawdust/PVC/LDPE composites using different contents of Silane A-137, Silane A-1100, and MAPE.

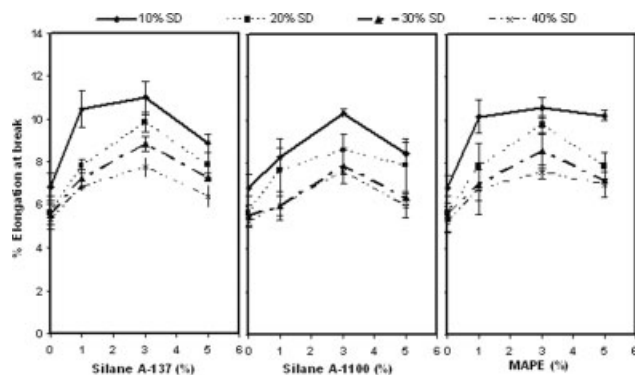
results of the composites reported in this work were obtained by averaging from 10 independent tested specimens. Tensile test was conducted according to ASTM D-638. The tensile measurements from dumbbell specimens were carried out using Universal Testing Machine (LLOYD Instrument, LR 5k) using WINDAP software with 5 kN load cell and a cross-head speed of 5 mm/min. Izod impact tester (Yasuda Seiki Seisakusho, 258-PC) was used to evaluate the impact strength of the blends and the composites. The notched testing specimens were used, following the ASTM D-256. The impact property results were reported in terms of impact energy divided by the area of the specimen ( $\text{kJ/m}^2$ ).

### SEM investigations

A LEO 1455 VP scanning electron microscopy was employed to study the interfacial morphology of the PVC/LDPE blends reinforced by wood fibers. The samples were immersed in a nitrogen liquid before fractured. After that the samples were sputter-coated with a thin layer of gold to prevent electrical charging during the observation. The surface characteris-



**Figure 2** Tensile strength of the sawdust/PVC/LDPE composites using different contents of Silane A-137, Silane A-1100, and MAPE.



**Figure 3** Elongation at break of the sawdust/PVC/LDPE composites using different contents of Silane A-137, Silane A-1100, and MAPE.

tics were examined and operated at 6 kV accelerating voltage.

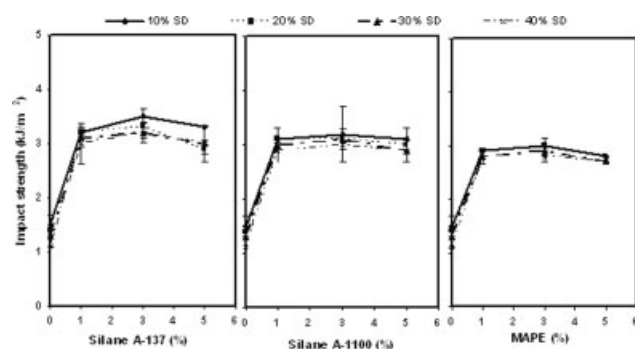
### Thermal properties

Glass transition temperatures of the samples were evaluated using a shear-bending mode dynamic mechanical analyzer (DMA, Merrier Teledo DMA/SDTA 861) at a temperature range from 20 to 130°C with a heating rate of 4°C/min and a fixed frequency of 1 Hz.

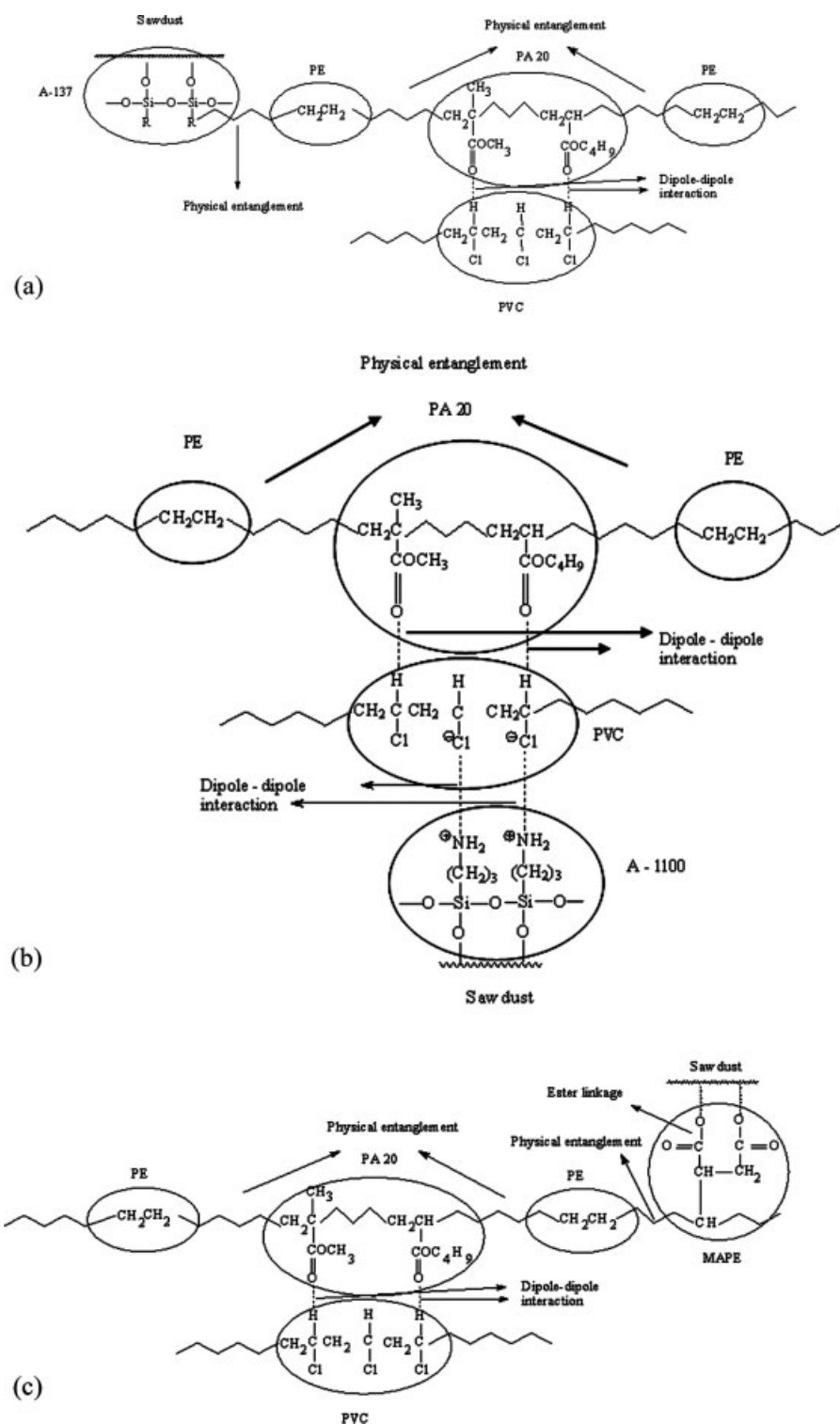
## RESULTS AND DISCUSSION

### Effect of coupling agents on mechanical properties

Mechanical properties of the wood-PVC/LDPE composites for different wood and coupling agent contents are shown in Figures 1–4. It can be seen that Young's modulus (Fig. 1) increased with increasing wood contents while the opposite effect was observed for the ultimate properties, i.e., tensile strength, elongation at break and impact strength (Figs. 2–4). These two effects were related to an increase in stiffness of the composites, and the dis-



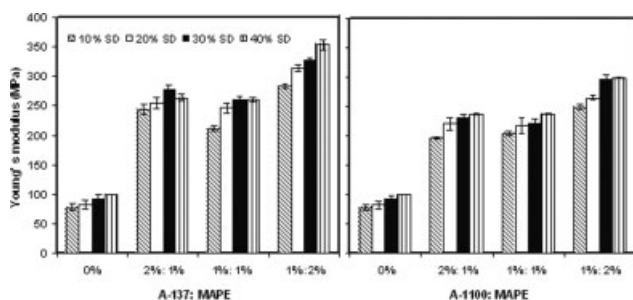
**Figure 4** Impact strength of the sawdust/PVC/LDPE composites using different contents of Silane A-137, Silane A-1100, and MAPE.



**Figure 5** Schematic diagram of the proposed interactions of the sawdust/PVC/LDPE composites using (a) Silane A-137 (b) Silane A-1100, and (c) MAPE.

continuity of the polymer phases in the composite samples, respectively. The obtained results were in good agreement with other research reports,<sup>9–17</sup> showing that coupling agents such as Silane or MAPE caused the improvement in mechanical properties of cellulose fiber-homopolymer composites.

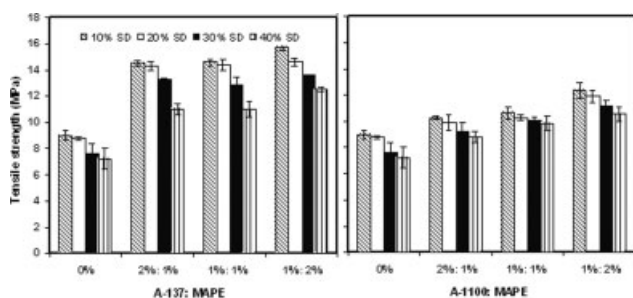
Considering the effect of type and content of coupling agents, it was observed that tensile and impact properties of the composites (Figs. 1–4) tended to increase with increasing the coupling agents, and then decrease at higher loading of the coupling agents. The results showed that the addition of low



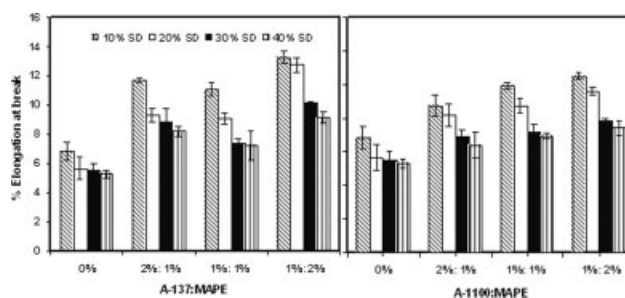
**Figure 6** Young's modulus of the sawdust/PVC/LDPE composites using different ratios of Silane A-137 : MAPE and Silane A-1100 : MAPE.

Silane or MAPE loading improved the mechanical properties of the composites. This was due to chemical interactions between each coupling agent and PVC/LDPE blend as shown and will be detailed later in Figure 5. On the contrary, higher loadings of Silane and MAPE brought about a reduction in the mechanical properties. This may be because of a self-condensation reaction of the Silane coupling agent.<sup>4</sup> The results were in line with those reported by Sombatsompop et al.<sup>5</sup> who used MAPP coupling agent in PP/wood sawdust composites.

When different coupling agent types were compared, MAPE and Silane A-137 were found to give better improvement than Silane A-1100. The dosages to give optimum mechanical properties for these three coupling agents were different, 3.0% for MAPE and 1.0% for Silane A-137 and Silane A-1100. The differences in required dosages may be related to levels of modifications and interactions of the coupling agents in the composites. The schematic diagrams of chemical and physical interactions between the PVC/LDPE matrix and the wood fiber reinforcement through the use of Silane coupling agents or MAPE are proposed in Figure 5. In the case of Silane A-137 (hydrocarbon silane) shown in Figure 5(a), Si—O-sawdust chemical bond can be formed between the coupling agent and the wood surfaces. Besides, the physical entanglement was likely to occur between the hydrocarbon chain-ends of Silane



**Figure 7** Tensile strength of the sawdust/PVC/LDPE composites using different ratios of Silane A-137 : MAPE and Silane A-1100 : MAPE.

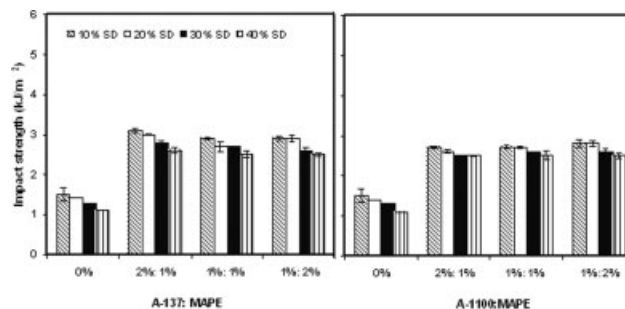


**Figure 8** Elongation at break of the sawdust/PVC/LDPE composites using different ratios of Silane A-137 : MAPE and Silane A-1100 : MAPE.

A-137 and the PVC/LDPE blend. Similar schematic reactions for kenaf fiber reinforced PP composites modified by silane coupling agent were reported by Karnani et al.<sup>10</sup> Similar to Silane A-137, the silanol groups in the Silane A-1100 coupling agent (amino silane) and hydroxyl groups can form chemical linkage between the coupling agent and the wood surfaces as shown in Figure 5(b). However, neither the amino groups nor the hydroxyl groups at the both ends of the Silane A-1100 molecules can entangle with PVC/LDPE phases. Figure 5(c) shows that MAPE coupling agent contains anhydride polar groups and PE nonpolar part and the polar anhydride groups can form ester linkages with wood surfaces via strong covalent bonds while nonpolar long-chain PE can perform physical entanglement with LDPE in PVC/LDPE matrix.<sup>17</sup>

#### Effect of Silane : MAPE ratio on mechanical properties

The effect of the use of mixed Silane and MAPE was examined by varying different ratios of Silane : MAPE, i.e., 2% : 1%, 1% : 1%, and 1% : 2%; the total content of Silane and MAPE was maintained at 3.0% wt wood sawdust. It can be seen in Figures 6–9 that using both Silane and MAPE caused a significant enhancement in mechanical properties of the wood-PVC/LDPE composites. According to the results and



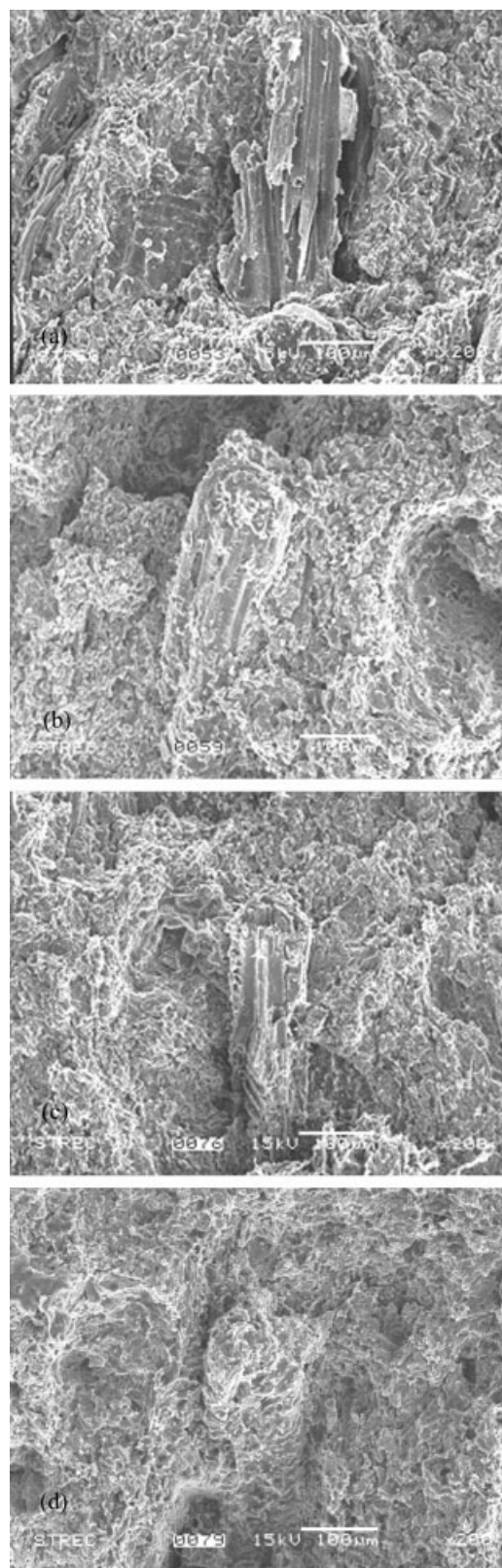
**Figure 9** Impact strength of the sawdust/PVC/LDPE composites using different ratios of Silane A-137 : MAPE and Silane A-1100 : MAPE.

explanations given when using single coupling agent in Figure 5, the use of mixed Silane A-137 : MAPE or mixed Silane A-1100 : MAPE still caused the physical and chemical linkages in different active sites. For mixed Silane A-137 : MAPE, chemical linkages between silanol and hydroxyl groups could be formed on the polar ends of Silane A-137 with the sawdust surfaces, and the covalent bonds by ester linkages were given via anhydride part in MAPE and hydroxyl groups in the sawdust. At the same time, the physical entanglement was obtained on the nonpolar ends of mixed Silane A-137 and MAPE with the PVC/LDPE matrix. For mixed Silane A-1100 : MAPE, the sawdust reinforcement interacted with the PVC/LDPE matrix by dipole–dipole interaction from Silane A-1100, and the physical entanglement and covalent bonds were caused by presence of MAPE. It should be noted that the physical entanglement could not be obtained between the Silane A-1100 and the PVC/LDPE matrix because the chain ends of the Silane A-1100 molecules are polar, leading to less physical interaction between the matrix and the reinforcement, compared with that of using both Silane A-137 and MAPE. This explanation suggested that the mixed Silane A-137 : MAPE resulted in better improvement in the mechanical properties of the composites than the mixed Silane A-1100 : MAPE. These statements were consistent with changes in the mechanical properties of the composite using Silane A-137, Silane A-1100, or MAPE alone (Figs. 1–4).

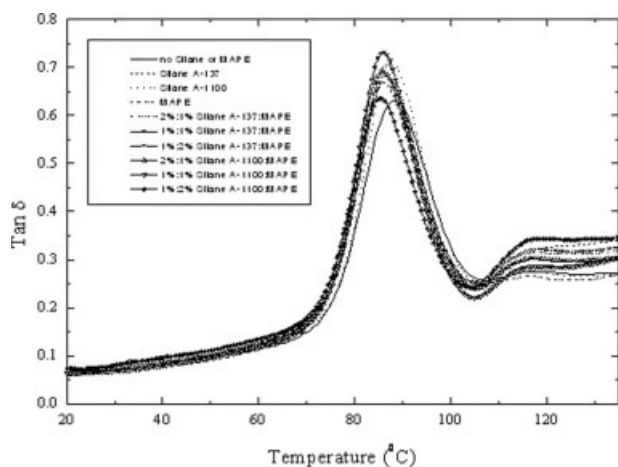
When different ratio of mixed Silane A-137 : MAPE and mixed Silane-A-1100 : MAPE were taken into account, the highest amount of MAPE (in the ratio of 1% : 2% Silane : MAPE) could give the optimum mechanical properties of the composites. It was postulated that by the presence of MAPE the possibility of the self-condensation reaction in Silane A-137 became minimized, thus leading to higher active sites of the Silane to interact with the PVC/LDPE matrix and the sawdust reinforcement. This implied that the composites with mixed Silane A-137 : MAPE at the ratio of 1% : 2% had greater overall mechanical properties than those with MAPE at 3% wt alone.

#### Effect of Silane or MAPE on morphological properties

Morphological properties of the Sawdust/PVC/LDPE composites are shown in Figure 10. It can be seen in Figure 10(a) that the matrix of PVC and LDPE blend compatibilized by PA20 was rather rough because high amount of LDPE (40 phr) was added into the PVC phase. Besides, the wood sawdust dispersed in the matrix phase of PVC/LDPE blend showed poor interfacial adhesion. When using



**Figure 10** SEM micrographs of the sawdust/PVC/LDPE composites using (a) no Silane or MAPE, (b) Silane A-137, (c) Silane A-1100, and (d) MAPE.



**Figure 11** Tan  $\delta$  of the sawdust/PVC/LDPE composites using different types and ratios of Silane or MAPE.

Silane A-137, Silane A-1100, or MAPE, the SEM micrographs in Figure 10(b–d) suggested that wetting phenomena was obtained, i.e., the wood particles were covered by the PVC/LDPE polymer matrix phase, indicating an improvement of the interfacial adhesion between the PVC/LDPE matrix and the wood reinforcement. It should be mentioned that the composites with MAPE showed the best wetting behavior. The morphological results were in line with the improvement of mechanical properties of the composites by the presence of the three coupling agents.

#### Effect of Silane and/or MAPE on thermal property

Thermal property of the sawdust/PVC/LDPE composites was examined using DMA technique through the loss tangent ( $\tan \delta$ ), which is defined as the ratio of the loss modulus to the storage modulus, and through the glass transition temperatures ( $T_g$ ), which was obtained via the  $\tan \delta$  peak. The relationships between  $\tan \delta_{\max}$  with temperature of the composites using Silane and/or MAPE are shown in Figure 11.

It was found that the  $\tan \delta_{\max}$  decreased with addition of the three coupling agents. The decrease in  $\tan \delta$  indicates the reinforcement occurring in the composites and this supported the improvement of the mechanical properties of the composites as discussed earlier. The  $T_g$  values of PVC of the different composite samples obtained from DMA technique are shown in Table II. The results suggested that the composites treated with Silane A-137, Silane A-1100, or MAPE had slightly lower  $T_g$  than the untreated composites, but the  $T_g$  values did not change with varying types and contents of the coupling agents. The reason of the decreased  $T_g$  by the addition of Silane A-137, Silane A-1100, or MAPE coupling agents was probably associated with the weakening of dipole–dipole interaction between the PVC and wood sawdust by the presence of these coupling agents.

## CONCLUSIONS

Composites from PVC/LDPE blend reinforced by rubber-wood sawdust were prepared and modified using three different coupling agents (Silane A-137, Silane A-1100, or MAPE). The effects of wood sawdust content, Silane, or MAPE content and the ratio of Silane : MAPE were examined. The experimental results suggested that tensile modulus increased with increasing wood contents, but the opposite effect was observed for tensile strength, elongation at break, and impact strength. The overall mechanical properties of the composites were improved with addition of Silane or MAPE coupling agent; Silane A-137 and MAPE coupling agents showed greater effect on mechanical property enhancement than Silane A-1100 coupling agent. The experimental results suggested that the composites with mixed Silane A-137 : MAPE at the ratio of 1% : 2% had greater overall mechanical properties than those with MAPE at 3% wt alone. In addition, the slight decreases in  $T_g$  and  $\tan \delta_{\max}$  values of the composites with Silane A-137, Silane A-1100, or MAPE were observed.

**TABLE II**  
Glass Transition Temperatures ( $T_g$ ) of the Sawdust/PVC/LDPE Composites Using Different Types and Ratios of Silane or MAPE

Samples	$T_g$ (°C)
PVC/LDPE/PA20/SD	88.2
PVC/LDPE/PA20/SD + Silane A-137	86.5
PVC/LDPE/PA20/SD + Silane A-1100	87.4
PVC/LDPE/PA20/SD + MAPE	86.0
PVC/LDPE/PA20/SD + (2% : 1%) Silane A-137 : MAPE	86.3
PVC/LDPE/PA20/SD + (1% : 1%) Silane A-137 : MAPE	86.5
PVC/LDPE/PA20/SD + (1% : 2%) Silane A-137 : MAPE	86.4
PVC/LDPE/PA20/SD + (2% : 1%) Silane A-1100 : MAPE	85.8
PVC/LDPE/PA20/SD + (1% : 1%) Silane A-1100 : MAPE	85.8
PVC/LDPE/PA20/SD + (1% : 2%) Silane A-1100 : MAPE	85.3

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### References

1. Miles, I. S.; Rostami, S. In *Multicomponent Polymer Systems*; Longman Scientific and Technical: London, 1992.
2. Prachayawarakorn, J.; Khamsri, J.; Chaochanchaikul, K.; Sombatsompop, N. *J Appl Polym Sci* 2006, 102, 598.
3. Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
4. Sombatsompop, N.; Chaochanchaikul, K. *J Appl Polym Sci* 2005, 96, 213.
5. Sombatsompop, N.; Yotinwattanakumtorn, C.; Thongpin, C. *J Appl Polym Sci* 2005, 97, 475.
6. Bikiaris, D.; Matzinos, P.; Larena, A.; Flaris, V.; Panayiotou, C. *J Appl Polym Sci* 2001, 81, 701.
7. Matias, M. C.; Orden, M. U.; Sanchez, C. G.; Urreaga, J. M. *J Appl Polym Sci* 2000, 75, 256.
8. Coutinho, F. M. B.; Costa, T. H. S.; Carvalho, D. L. *J Appl Polym Sci* 1997, 65, 1227.
9. Rozman, H. D.; Kon B. K.; Abusamah, A.; Kumar, R. N. *J Appl Polym Sci* 1993 1998, 69.
10. Karnani, R.; Krishnan, M.; Narayan, R. *Polym Eng Sci* 1997, 37, 476.
11. Keener, T. J.; Stuart, R. K.; Brown, T. K. *Compos A* 2004, 35, 357.
12. Harper, D.; Wolcott, M. *Compos A* 2004, 35, 385.
13. Marcovich, N. E.; Villar, M. A. *J Appl Polym Sci* 2003, 90, 2775.
14. Zhang, F.; Endo, T.; Qiu, W.; Yang, L.; Hirotsu, T. *J Appl Polym Sci* 2002, 84, 1971.
15. Colom, X.; Carrasco, F.; Pages, P.; Canavate, J. *Compos Sci Technol* 2003, 63, 161.
16. Balasuriya, P. W.; Ye, L.; Mai, Y.-W.; Wu, J. *J Appl Polym Sci* 2002, 83, 2505.
17. Felix, J. M.; Gatenholm, P. *J Appl Polym Sci* 1991, 42, 609.