[AMN08] Effect of the silane coupling agent on the hybrid thermoplastic natural rubber composites filled rice husk and oil palm empty fruit bunch

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Introduction

The used of lignocellulosic material as replacement in composites is currently generating much interest in most application. Lignocellulosic-derived fillers have many advantages compared to inorganic fillers. The advantages of natural filler receiving increasing attention for industrial application due to cost effectiveness, low density, high specific strength, bio-degradability and free from health hazard (Baiardo et al. 2002; Thwe & Liao 2002). According to Mohd Ishak et al. (1998), these materials have greater deformability, flexibility during processing and derived from renewable resources.

Hybridisation of the natural fiber that contains two or more fillers is the advantages of one type of filler could complement what are lacking in other (Thwe & Liao 2002). In this study, the used of RH filler and EFB fiber have twofold:- one is to reduce the cost of expensive synthetic filler using rice husk and the other is utilize the inherent reinforcing fiber that can counterbalance RH weaknesses.

In general, mechanical of the composites basically depend on strength and modulus of the fillers, strength and toughness of the matrix and efficiency of interfacial stress transferred (Rong et al. 2001). However natural filler suffer from lower modulus, lower strength, and relatively poor moisture resistance compared to synthetic fillers. This may be contributed to insufficient adhesion between fillers and polymer matrix which leads debonding with age (Gassan et al.1997). The moisture uptake is very high to these filler because the presence of the hydroxyl and other polar group in various constituents of natural filler. Therefore, it contributed to weak interfacial bonding between filler and hydrophobic polymer matrix, thus compromising the mechanical properties of composites (Thwe & Liao 2001). Most attempt to overcome this situation is y grafting the coupling agent with compatibilizer onto the filler. Therefore, hydrophilic natural fillers and hydrophobic matrix can be coupled together with coupling agent or comptibilizer acting as a bridge between them.

In these studies, the behavior of the composites hybrid of RH and EFB fiber in TPNR matrix with the presence of the silane coupling agent and MAPE as a compatibilizer were investigated.

Materials and Methods

Materials

The SMR-L natural rubber (NR) was obtained from Guthrie (M) Sdn. Bhd.; Liquid natural rubber was prepared in UKM Materials Science Program and HDPE powder form with $0.97cm^{-3}$ density was supplied by Petrochemical (M) Sdn. Bhd. RH was supplied by Bernas Sdn. Bhd. and then was refined to the size of 300 µm. EFB fiber was obtained from Sabutek Sdn. Bhd. The EFB fibers were also refined to the 150µm width with 1300-1800µm length. Silane (Z 6020) coupling agent was supplied by Dow Corning Corp. Michigan (USA) and MAPE (Maleic Anhydride grafted-Polyrthylene) was supplied by Aldrich Chemical Company, Inc. (USA).

Sample Preparation

Blends of TPNR matrix were first prepared with composition ratio of NR: LNR: HDPE are 20:10:70 vol. % via internal mixer. The blending was carried out at 135ºC for 13 minutes at 50 rpm. Following this, the blending of hybrid composites was prepared at 145ºC for 13 minutes at 50 rpm. RH filler and EFB fiber were hybrid into TPNR matrix at various compositions; RH/EFB: 0/25, 5/20, 10/15, 15/10, 20/5 and 25/0 vol. %. RH filler was treated using silane coupling agent before incorporated into matrix. TPNR matrix was allowed to melt for 3 minutes in the mixer before introducing MAPE. TPNR and MAPE were allowed to mix 1 minute before the fillers were charge into the mixer.

Tensile test was carried out on five sets of samples for each composite according to ASTM D 412 using Testometric Instument. Five sets of sample for impact test were also prepared according to ASTM 256-93 using Universal Fractoscope. The absorption behavior was tested by soaking composites samples into distilled water for one week. The observation was done for first and seventh day and the increasing of the mass was determined. Composites were test using Shore D tester to study the hardness of the composites. Fractured surface of the tensile test composites was observed using scanning electron microscope (SEM) to study the interaction capability between the matrix and fillers.

Result and Discussion

Tensile strength

Figure 1 shows the effect of the silane coupling agent and MAPE on the tensile strength of RH-EFB hybrid composites. It can be observed that there no significance enhancement on tensile strength by hybridization of the RH and EFB fiber without the presence of the silane and MAPE. Micrograph SEM in Figure 7 shows the lack adhesion between filler and TPNR matrix without the presence of silane coupling agent and MAPE. Thus, the capability to support stress transmitted from TPNR matrix is rather poor.

However, value of the tensile strength has increased slightly with the presence of the silane coupling agent. This may be attributed to the diamine organofunctional group in silane caused reaction with polymer matrix. It could be a copolymerization and/or formation of an interpenetrating network. This curing reaction of a silane-treated subtract enhances the wetting by resin (Bledzki et al. 1996).

A significance improvement of the tensile strength has been obtained with the presence of the MAPE. The used of compatibilizer has improved the wetting ability dispersion that will result in good mechanical strength. The presence of compatibilizer shown an enhancement on tensile strength is believed has improved surface functionality of EFB fiber and enabled to form chemical bonding with TPNR matrix. Maleic Anhydride (MA) containing carbon-carbon double bond (C=C) and two carboxylate group (-COO-). These conjugate structures greatly increase the graft reactivity with the polymer matrix resulting in cross-linking or strong adhesion at interface (Lu et al. 2000). The combined effect of silane treatment and the addition of MAPE shows higher increasing on tensile properties are expected. It can be proved by strong adhesion in SEM micrograph in figure 8.

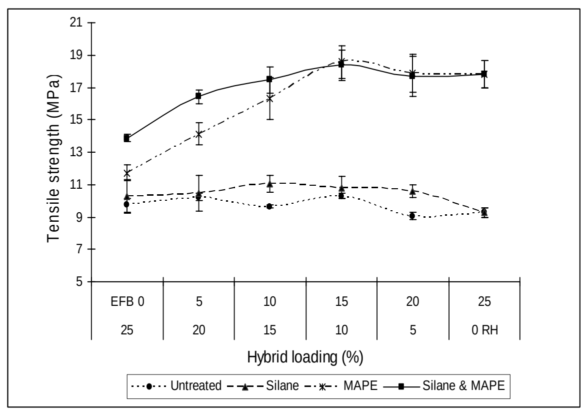

FIGURE 1 Effect of the coupling agent and compatibilizer on tensile strength of RH-EFB hybrid composites.

Maximum strain

Effect of the coupling agent and compatibilizer on the hybrid composites can be observed in figure 2. The addition of MAPE and silane treatment on RH not shows significance different in strain properties. Lower in maximum strain value attributed to the presence of the silane and MAPE. These coupling agent and compatibilizer tend to expose extra resistance to flow and lead lower resistance to break. However, the increasing of EFB fiber loading resulted in a drastic reduction on maximum strain. The decreased in strain properties with the increasing of EFB loading indicates hindrance by EFB to molecular mobility or deformability of TPNR blends (Ismail et al., 2001). Futhermore, RH filler is highly brittle as compared to EFB fiber. The stiffness properties of RH filler will reduce the composite resilience and toughness and lead to lower elongation at break.

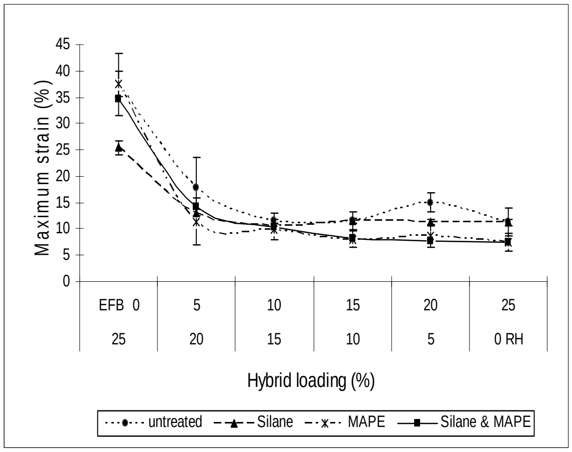

FIGURE 2 Effect of the hybridization of RH-EFB on maximum strain of the composites.

Stiffness

Comparative effect of the silane coupling agent and MAPE on the stiffness properties have been presented on Figure 3. Similar to the tensile strength, hybridization of RH and EFB fiber into composites system without silane and MAPE not shows increasing in stiffness properties. Value of the Young's Modulus has increase slightly with silane treatment. The presence of the silane has led to an enhancement on the filler matrix interfacial bonding.

The addition of MAPE caused an increasing trend in Young's Modulus represent higher stiffness of the composites. As discussed earlier, the presence of the MAPE may attribute to the improvement in the filler matrix bonding. It can be seen that the trend increasing with EFB loading. This contributed to capability EFB fiber to impart greater stiffness on the matrix. According to Rozman and his friends (1998), the length and aspect ratio of the fiber could enhance the stiffness of the composites. This fiber effective reinforcing capability could be attributed to it microfibrilliar and hollow nature and the irregular shape of their cross section

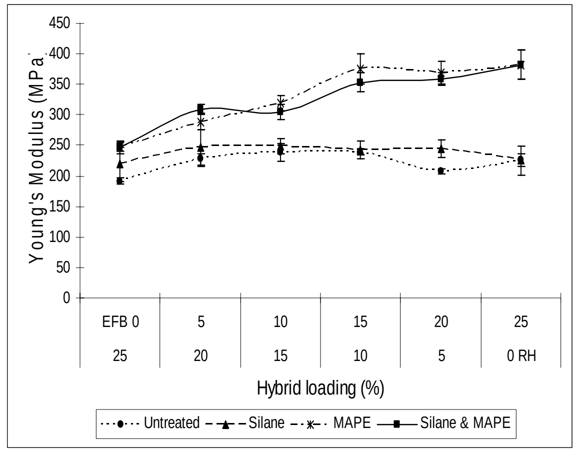

FIGURE 3 Comparative effect of the silane coupling agent and compatibilizer on the stiffness of RH-EFB composites.

The presence of MAPE into TPNR matrix has increase the stiffness of the matrix. As discuss earlier, this may be attributed to the improvement in the EFB- matrix adhesion which lead to an increasing of efficiency of the stress transferred from the matrix to the EFB fiber. Lower stiffness of the hybrid composite with higher RH content resulted from presence of the high silica content on the RH surface.

Impact Strength

Figure 5 show effect hybridization of the RH and EFB fiber on impact properties of hybrid composite. It can be seen that hardness increasing with increasing of the EFB content. One of the main factor affecting hardness properties of composites is the ability of the filler to absorb impact energy before crack. With higher aspect ratio of filler, EFB tend to absorb more energy transmitted from the matrix along the fibers before crack.

MAPE is able to impart greater stiffness in the matrix while silane is only show a slightly improvement. The presence of the MAPE in the TPNR matrix caused higher restriction of the molecular motion of the macro-molecules.

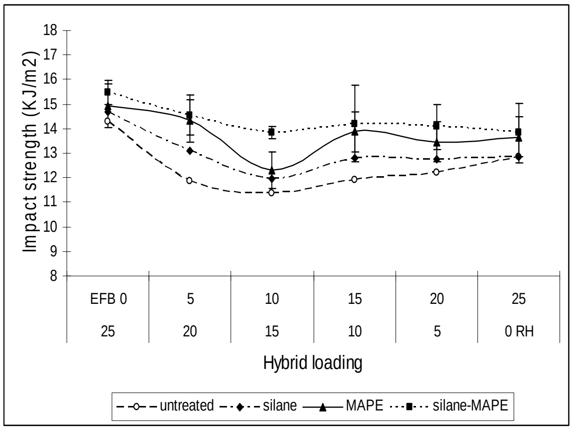

FIGURE 4 Coupling agent and compatibilizer dependence of impact strength of RH-EFB hybrid composites.

Hardness

Effect of the hybridization of RH and EFB and the presence of the coupling agent and compatibilizer can be seen on the Figure 5. The increasing of the EFB fiber loading in TPNR matrix resulted and stiffer harder composites. This may be attributed by decreasing deformability rigid interface of the matrix component with increasing of the EFB fiber.

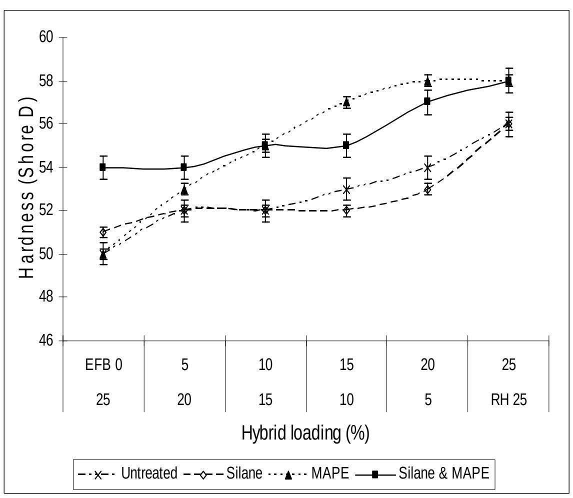

FIGURE 5 Hardness of the hybrid composites with the presence of the silane coupling agent and MAPE.

The treatment of the silane coupling agent on the RH surface not has shown significance influence on hardness properties. However, the presence of the MAPE exhibit higher hardness than silane treatment. As discussed earlier, this may be attributed to the improvement in the filler-matrix bonding. The presence of the MAPE leads the higher efficiency of stress transferred from the matrix to the filler phase (Ismail et al 2001).

Water absorption

The absorption curve of hybrid composites after soaking in distilled water of 25ºC within one week are shown in Figure 6. It can be seen that higher content of EFB fiber tend to absorb water than RH filler. Hygroscopic properties of EFB fiber could be the reason of the increasing absorption water in composites hybrid with higher EFB content compare to the RH. Further more, with the aging of the exposure to the moisture has reduced water resistance. The higher resistance absorption behavior has been obtained with increasing of RH filler loading. This may be due to the higher silica content on the RH surface which could prevent water from penetrating RH filler.

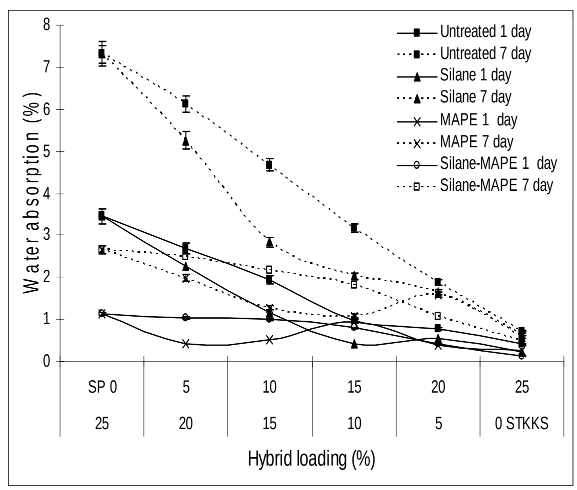

FIGURE 6 Sorption behavior of hybrid composites within 1 week.

However, with the incorporation of the MAPE compatibilizer has decreased in water absorption behavior. Water resistant increased in about 63% in higher EFB content with the presence of MAPE. The improve moisture resistance caused by the application of the coupling agent and compatibilizer can be explain by fiber matrix adhesion (Bledzki et al. 1999). The reduction in moisture level is attributed to the improved interfacial adhesion that reduced water accumulation in the interfacial void and prevents water from entering the fillers (Thwe & Liao 2003).

Morphology

SEM micrograph of the tensile fracture surfaces of hybrid composites are shown in Figure 7. The polarity of the wood filler is obviously not capable to form a good filler-matrix interaction with non-polar matrix of TPNR. This indicates the lack of the adhesion between filler and polymer matrix. As expected, this factor contributed to the lower tensile strength which can be observed in Figure 1.

Figure 8 show the distribution of the RH and EFB filler with the presence of the silane and MAPE. It was indicated that an improvement of interaction bonding between RH and EFB with TPNR matrix. These agents may improve the better dispersion of the filler in composites. Enhancement of mechanical properties could only be achieved if there is a good dispersion and wetting of the fiber in the matrix that will give a rise to strong interfacial adhesion. It believe that the presence of the functional group in MAPE and silane play significance role to increase interaction and compatibility with TPNR matrix.

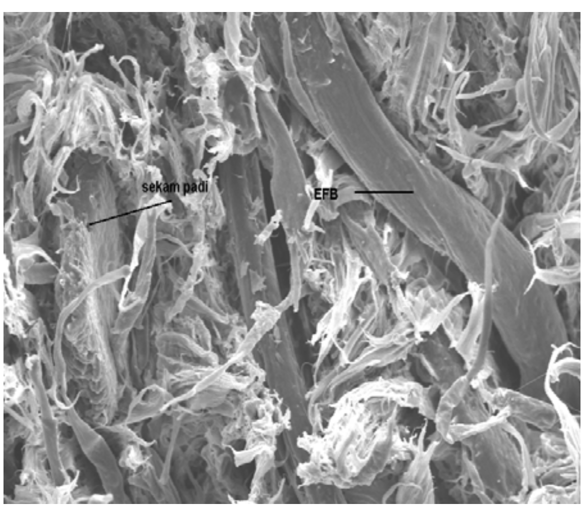

FIGURE 7 SEM micrograph of hybrid composites without coupling agent and compatibilizer.

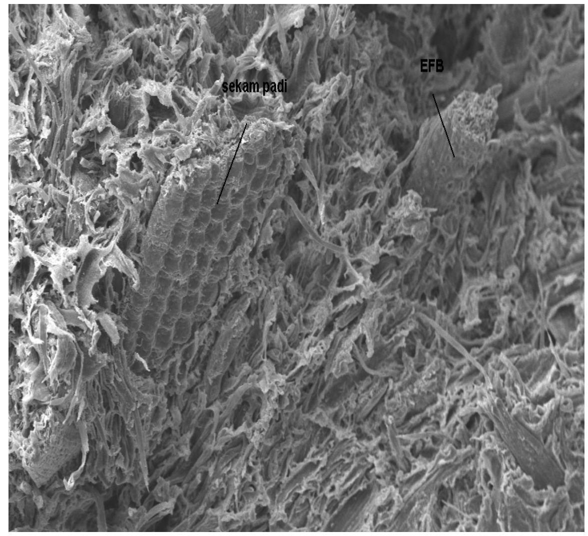

FIGURE 8 SEM micrograph of hybrid composites without with silane and MAPE.

Conclusion

Hybrid composites were fabricated with hybridization RH and EFB fiber with the presence of silane coupling agent and MAPE as a compatibilizer. Tensile strength, stiffness and hardness properties have been increased by increasing of the EFB content. However, the increasing of the EFB fiber has decreased maximum strain and water absorption properties. Incorporation of the EFB fiber can counterbalance RH properties. Unfortunately, RH only can be used to reduce TPNR matrix. The presence of the MAPE could improve mechanical properties in RH-EFB hybrid composites compare to the presence of the silane. Tensile, impact, hardness and sorption behavior results greatest enhancement with the presence of this compatibilizer.

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