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EFFECT OF FIBER SURFACE CHEMISTRY ON THE MECHANICAL PROPERTIES OF GLASS FIBER MAT REINFORCED THERMOPLASTIC NATURAL RUBBER (TPNR) COMPOSITES

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Abstract. The mechanical properties of thermoplastic natural rubber (TPNR) reinforced by glass fiber mat were examined as a function of the chemical functionality of the silane surface treatment applied to the glass fiber mat. The TPNR was a blend of high density polyethylene, natural rubber and liquid natural rubber at a HDPE/NR/LNR ratio of 50:40:10 which was compounded using an internal mixer. The results indicate that silane coupling agent improved the mechanical properties of the composite. The peel test showed an increment of torque values from 0 to 15% silane concentration. The results also showed that tensile properties and impact absorption energy increased with silane concentration with the optimum concentration were found to be at 15%. However, hardness data exhibited no significant difference with the increment of silane concentration. The investigation of the morphological for the sample through scanning electron microscopy (SEM) also showed that the adhesion between the glass fiber mat and the NR/HDPE matrix improved with silane concentration.

Key words: glass fiber mat, natural rubber, polyethylene, coupling agent

Abstrak. Sifat mekanik termoplastik getah asli (TPNR) yang diperkuat gentian kaca tikar telah dikaji berfungsikan rawatan permukaan gentian kaca tikar menggunakan silana. TPNR yang digunakan adalah adunan polietilena berketumpatan tinggi (HDPE), getah asli (NR) dan cecair getah asli (LNR) pada nisbah HDPE/NR/LNR 50:40:10 yang telah diadun menggunakan mesin pengadun dalam. Keputusan menunjukkan bahawa agen pengkupelan silana telah memperbaiki sifat mekanik komposit. Ujian koyak menunjukkan peningkatan nilai tork daripada 0 hingga 15% kepekatan silana. Keputusan juga menunjukkan bahawa sifat regangan dan tenaga penyerapan hentaman didapati telah meningkat dengan kepekatan silana di mana kepekatan yang optimum adalah 15%. Bagaimanapun, data kekerasan tidak menunjukkan sebarang perubahan yang ketara dengan peningkatan kepekatan silana. Pemeriksaan morfologi terhadap sampel menggunakan mikroskop imbasan elektron juga menunjukkan bahawa perlekatan antara gentian kaca tikar dan matriks NR/HDPE telah meningkat dengan peningkatan kepekatan silana.

Kata kunci: Gentian kaca tikar, getah asli, polietilena, agen pengkupelan

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1.0 INTRODUCTION

The addition of glass fiber mat reinforcement is known to improve the stiffness, strength, and the high temperature performance of polymeric materials [1,2]. The mechanical properties of the resulting glass fiber mat reinforced composite materials depend heavily on the nature of the fiber-matrix interface. When a load is applied to a fiber-reinforced composite, the load is transferred between the low-modulus matrix and high-modulus fiber through the interface.

Rubber-toughening, on the other hand, is used to improve the impact properties and low temperature toughness of the polymer. Physical blends of natural rubber (NR) and polyolefin that form a thermoplastic natural rubber (TPNR) have also been developed into a semi-rigid plastic. To overcome the incompatibility, the mixing of thermoplastic and natural rubber requires compatibilizer that can induce interactions within the phases or at the interface. Previous studies on TPNR include the work by Ibrahim & Dahlan [3] who studied the effect of liquid natural rubber (LNR) on the mechanical and morphological properties of the blend. They found that for the blend with the compositions around 50% NR, 10-15% LNR produced the most significant improvement in the physical properties.

Since the interface between the glass fiber mat and plastic is considerably weak, surface modification can improve mechanical properties by adding the silane coupling agent to glass fiber mat composites. By reacting with the polymer and modifies the morphology at the interface, silane coupling agent improve the stress transfer at interface and the resistance to water [4]. Silane coupling agent is compatible with almost every type of organic polymer, ranging from thermosetting resins through elastomers to thermoplastic resins [5]. Therefore, silane coupling agent has maximum reactivity with the polymer. The interaction between thermoplastic and glass fibers can be improved further by including additional cross-linking agents like co-reactants, polyfunctional monomers, peroxides and so on at the interface between the matrix polymer and the glass fibers [6].

In previous research, the effect of using silane coupling agent in PP reinforced with glass fiber mat was studied [7]. Further research by Laura *et al.,* [8] using different reactive silane coupling agents on glass fiber reinforced rubber-toughened nylon 6 showed that the mechanical properties are influenced by the functional group of silane.

In this paper, the mechanical properties of glass fiber mat reinforced TPNR composites had been investigated as a function of the silane concentration. Further more, the morphology investigations were performed using scanning electron microscopy (SEM).

2.0 EXPERIMENTAL

2.1 Materials

The matrix materials consist of natural rubber (NR), SMR-L type supplied by Rubber Research Institution Malaysia (RRIM) and high density polyethylene (HDPE) purchased from Commercial Plastic Sdn Bhd. (M) with a density of 0.96 g/cm^3. Liquid natural rubber (LNR) was prepared in our Rubber Research Laboratory through photodegratation reaction as described elsewhere [9]. Glass fiber mat with a density of 2.5 g/cm^3 and thickness around 0.4 mm was supplied by Eurochem. N-(2-Aminoethyl)-3-aminopropyl-trimethoxy silane (APS) supplied by Merck-Schuchardt was used as coupling agent. For the preparation of silane solution, ethanol provided by R & M Chemicals Ltd. (UK) having molecular weight of 46.07 g/mol was used.

2.2 Specimen Fabrication

2.2.1 Glass Fiber Mat Treated

Different concentrations of silane solution were prepared by mixed the silane with ethanol and water (95:5) for a specific concentration based on volume percentage. The APS was hydrolysed for 5 minutes. Table 1 shows the volume of silane and the mixture solution of ethanol and water for the preparation of different silane concentration.

Glass fiber mat was dried in vacuum oven (GallenKamp) for 10 hours at 50˚C. The mat was then immersed into silane solution for five minutes and dried in vacuum oven for ten minutes at 110˚C.

Table 1 Volume of silane and mixture solution of ethanol and water for preparation of different concentrations silane

Silane Concentration (%)	**Silane (ml)**	**Mixture solution of ethanol and water (ml)**
5	5	95
10	10	90
15	15	85
20	20	80

2.2.3 Preparation of Samples

Blends of NR/HDPE/LNR with composition ratio of 40:50:10 were carried out in an internal mixer, HAAKE Rheomix, model CTW 100. At the beginning, NR was put into the blending machine operated at 135˚C and 55 rpm rotation rate for about one minute. LNR was then added after one minute for further mixing before HDPE was charged into the mixture. The total mixing process duration was 10 minutes. After that, the blend was pressed using hydraulic compressor (Carver, model 2697) into a piece of NR/HDPE blend with 1 mm thickness. Pressure imposed was 7 MPa for 15 to 20 minutes. The mat was then embedded and compression molded with NR/HDPE blend at 135˚C for 15-20 minutes following the method by Lee & Jang [10]. The volume fraction of glass fiber in the composite, V_f, was 0.15 and the thickness of specimens was 1 mm.

2.3 Testing and Characterizations

2.3.1 Peel Test

A simple instrument for peel tests had been modified in accordance to ASTM D 1781-76, a standard method for the peel resistance of adhesive bonds between the relatively flexible facing of a sandwich structure and its core. Peel test had been carried out to measure the adhesion strength between glass fiber mats and TPNR at various concentrations of silane coupling agents. This instrument was connected with the Testometric tensile machine and the forces used to tear the samples were recorded. All measurements were carried out at a crosshead speed of 50 mm/min. and, a torque-displacement curve was obtained. The specimen size was 25 mm wide and 1 mm thickness.

2.3.2 Tensile Test

Tensile properties were determined using a Testometric tensile machine (model M 350 – 10 kN) with a crosshead speed of 50 mm/min in accordance to ASTM D 638 – 91. The shapes of the samples were dumbbell shape with length and gauge widths were 75 mm and 4 mm respectively. Each sample thickness was measured at several different areas.

2.3.3 Impact Test

Izod impact test was conducted in accordance to ASTM D256-88. The size of notched specimens was 13 mm wide (h) and 60 mm long (L). The notch length (a) was 0.1 mm and the thickness of the samples (b) was 1 mm. The impact absorption energy, u_t was obtained by dividing the total absorbed energy, U_t, with the cross-sectional area of each specimen base on the following equation (Equation 1).

$$u_t = \frac{U_t}{b(h-a)} \tag{1}$$

2.3.4 Morphological Study

Morphologial study was carried out on samples after tensile test. The samples were sputter coated with gold-palladium and investigated using a Philips XL30 scanning electron microscope (SEM).

3.0 RESULTS AND DISCUSSION

3.1 Peel Test

A load-displacement curve for ideal peel test is shown in Figure 1. Based on the research on fiber-reinforced plastic (FRP)/natural rubber done by Jyongsik and Byungwon [11], the applied load increased to an arbitrary level depending on the adhesion properties of FRP/natural rubber before reaching a constant value. However, this research showed an inconsistently force (load) evacuation towards the interfacial region and the applied force was also liable to change after reaching the maximum load as shown in Figure 2. This situation can be explained by the elastic behavior of rubber presented in the composite. As a result, the force cannot be transferred towards the interfacial region consistently.

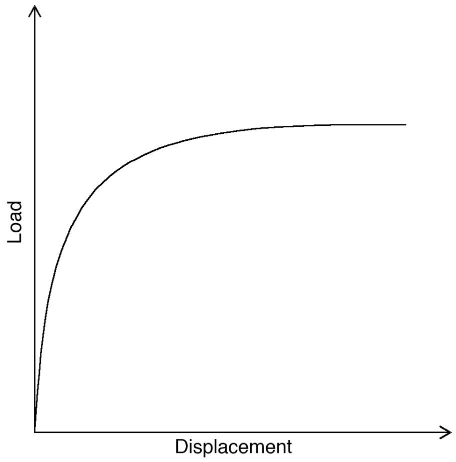

Figure 1 Load-displacement curve of the adhesive system in the ideal peel test

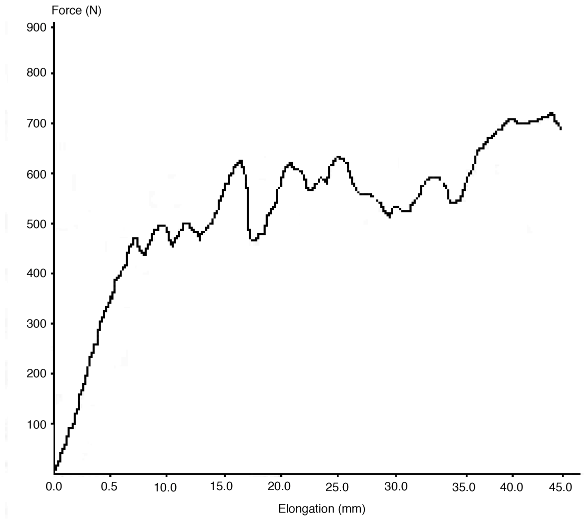

Figure 2 Typical load-displacement curve for glass fiber mats reinforced TPNR composites with different silane concentration

Each of the torque values shown in Figure 3 was the average of maximum force obtained from the force-elongation curve obtained from Figure 2. As shown in Figure 3 that the torque increased with the increase of silane concentration from 0% to 15%. Highest torque values for TPNR reinforced by glass fiber mat was 80.5 kN/m. Interfacial region between TPNR matrix and glass fiber mats was the critical and significant region where stress in shear must be distributed and transferred efficiency from low-modulus TPNR matrix resin to the high-modulus glass fiber mats. TPNR matrix resin could be bonded to the glass fiber mats by using a reactive silane and difunctional monomer at the interface. Cross-linking at the interface seemed to be a requirement for good adhesion. It can be seen in Figure 3, that there was a significant improvement of adhesion with increasing of silane concentration. This was because silane coupling agent acted as a cure material which was used to be modified the surface of polymer through co-polymerization in order to improve the adhesion strength between glass fiber mats and TPNR. Addition of cure material can induce the cross-linking between the polymer and also the adhesion strength of the polymer [12]. The results indicated that cross-linked between matrix and glass fibers layers was increased with silane concentration and followed by enhancement the peel strength of the composite. However, at high silane concentration, the unreacted curing agent remained as a separate and viscous phase at the matrix and glass fiber interface and finally caused the reduction in adhesion strength.

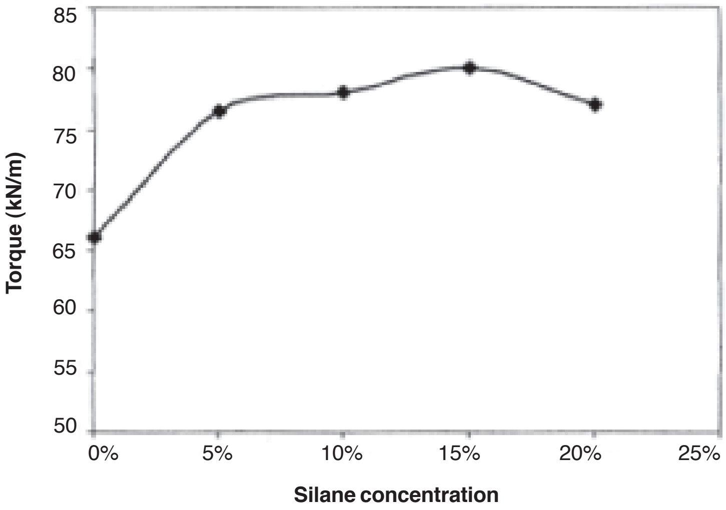

Figure 3 Effect of silane concentration in glass fiber mats reinforced TPNR composites on torque values obtained after peel test

3.2 Tensile Tests

Table 2 shows the tensile properties of TPNR reinforced with glass mat at different silane concentration. It can be seen that the tensile strength increased constantly with increasing of silane concentration from 0 to 15% and drop immediately at higher concentration. Similarly, there is also an improvement of strain at break from 0 to 15% silane concentration but the improvement is really small with only 11.81%. Table 2 also shows that the optimum value of tensile modulus is at 15%.

Table 2 Effect of silane concentration on tensile properties

Silane concentration (%)	Tensile strength (MPa)	Strain at break (%)	Tensile modulus (MPa)
0	12.5 ± 1.8	23.2 ± 2.2	38.5 + 1.2
5	14.0 ± 1.2	24.4 ± 1.8	46.8 + 2.8
10	13.6 ± 2.0	25.0 ± 1.0	61.5 + 3.0
15	18.8 ± 1.2	26.9 ± 2.0	70.3 + 3.2
20	8.6 ± 1.0	20.0 ± 1.6	43.7 + 2.8

The improvement of the tensile properties from 0 to 15% can be explained by the formation of semi-interpenetrating polymer network (semi-IPN) between NR/HDPE composite and silane. This situation could be induced strength of the interfacial bond between glass mat and TPNR matrix [13]. However, the reduction of tensile properties above 15% silane concentration will cause absorption of silane at glass surface without any chemical reaction and formation of semi-IPN.

3.3 Impact Absorption Energy

The impact absorption energy of TPNR composites reinforced glass fiber mat according to silane concentration is shown in Figure 4. It can be seen that the impact energy increased with concentration of silane treatment until 15% but decreased immediately when the concentration of silane is higher than 15%. The maximum value of impact absorption energy is 20.5 kJ/m^2. This research supports the "retrained layer" theory for silane-modified interfaces in polymer composites. The main sources of fracture absorption energy in glass fiber reinforced thermoplastic especially for reinforcement of long fibers were debonding at the interface, fiber pull-out and plastic deformation of the thermoplastic matrix [14]. This fact clearly explained that silane treatment would prevent the debonding and fiber pull-out processes, followed by the increasing of the impact energy when the specimens were broken. Consequently, the impact absorption energy will increase instantly.

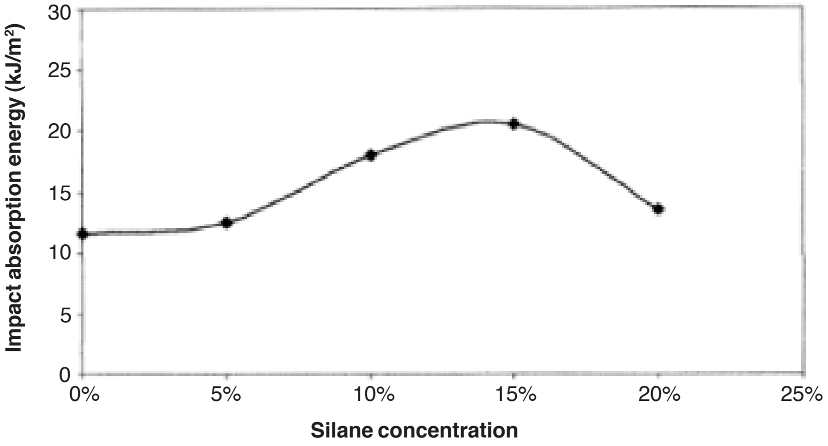

Figure 4 Effect of silane concentration in glass fiber mats reinforced TPNR composites on impact absorption energy

3.4 Hardness

Figure 5 shows the hardness value of TPNR composite as a function of silane concentration. The improvement of sample's hardness was equivalent with the increasing of silane concentration from 0% to 15%. However, the variation is not significant compared with the tensile properties and impact properties. The alternation of sample's hardness was inconspicuous with different silane concentration because the main factor that affected the sample's hardness is the composition of glass fiber mat in the composite. Meanwhile, silane coupling agent only promotes strong bonding at the interface. The volume fraction of glass fiber mat in the composite was constant at 0.15, which implies that the hardness of the composites only affected by the composition of glass fiber mat and not to the silane concentration. It can be seen that addition of silane coupling agent only improved the interfacial bonding between the matrix and glass fibers without giving any perceptible impression to the value of hardness.

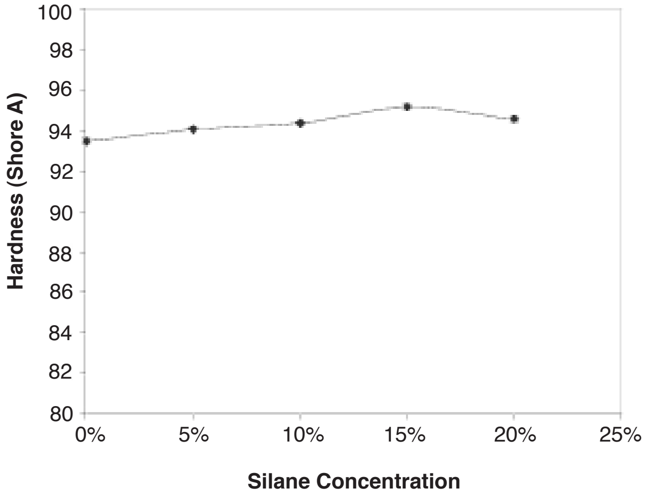

Figure 5 Effect of silane concentration in glass fiber mats reinforced TPNR composites on hardness

3.5 Morphological Investigation

Figure 6 shows the scanning electron micrograph of treated glass fiber mats with different silane concentration and untreated fiber in TPNR composites. It can be seen in Figure 6(a) that the surface of untreated fiber after tensile test was really smooth. From considerations of the extracted fiber it would appear that there was no bonding between glass fiber and TPNR matrix. The matrix adherences at the fiber surface show an increment from 0 to 15% silane concentration (Figure 6(a) – 6(d)). This analysis indicates that the adhesion between the matrix and glass fiber mats is significantly improved with the increasing of silane concentration.

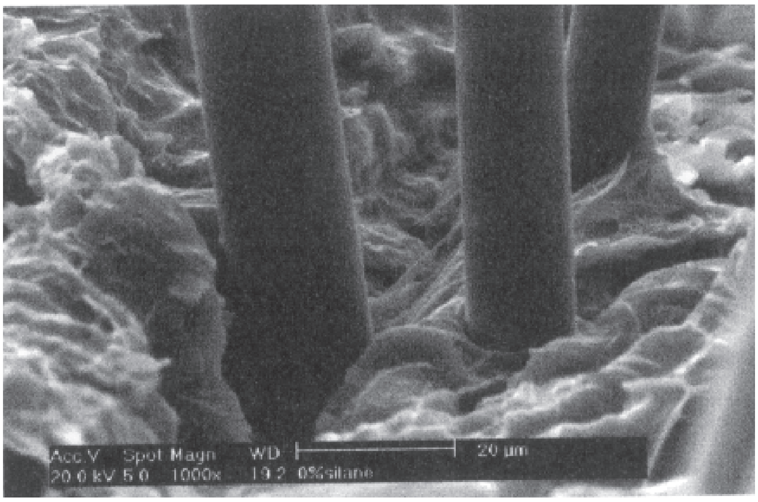

Figure 6(a) Scanning electron micrograph of tensile fracture surface of glass fiber mats reinforced TPNR composites treated with 0% silane concentration

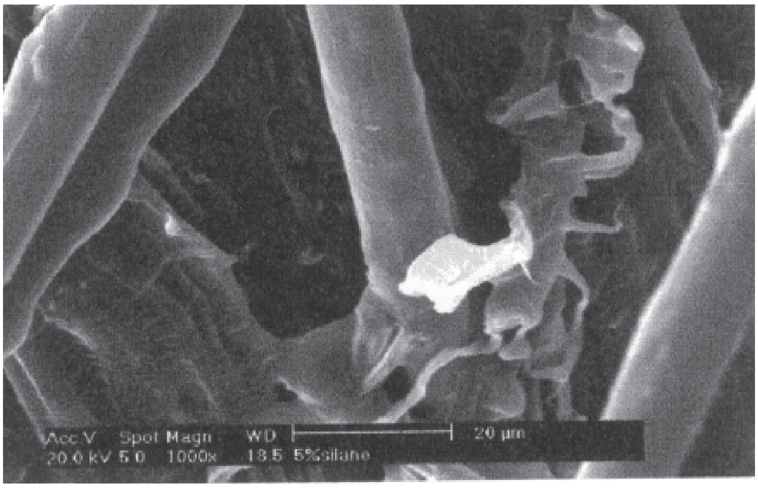

Figure 6(b) Scanning electron micrograph of tensile fracture surface of glass fiber mats reinforced TPNR composites treated with 5% silane concentration

However, the adhesion between TPNR matrix and glass fiber layers became weaker at 20% silane concentration (Figure 6(e)) which might be due to adsorption of silane affect at fiber surface without any semi-IPN and chemical reaction [15].

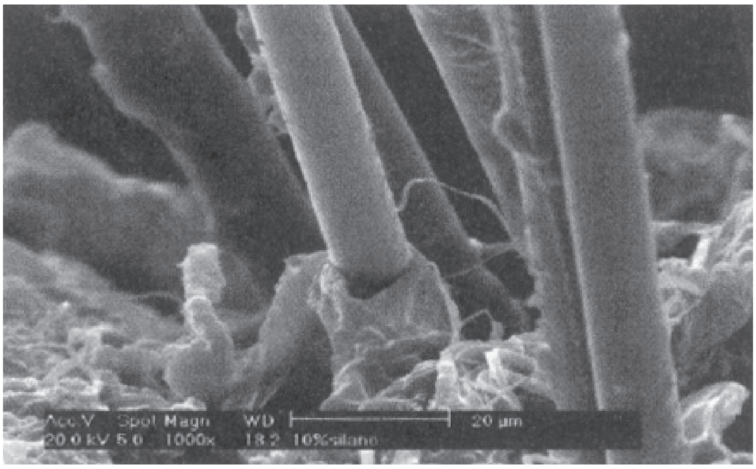

Figure 6(c) Scanning electron micrograph of tensile fracture surface of glass fiber mats reinforced TPNR composites treated with 10% silane concentration

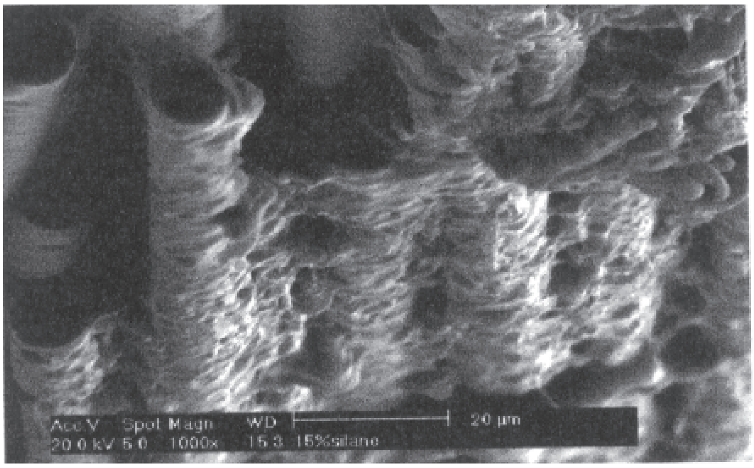

Figure 6(d) Scanning electron micrograph of tensile fracture surface of glass fiber mats reinforced TPNR composites treated with 15% silane concentration

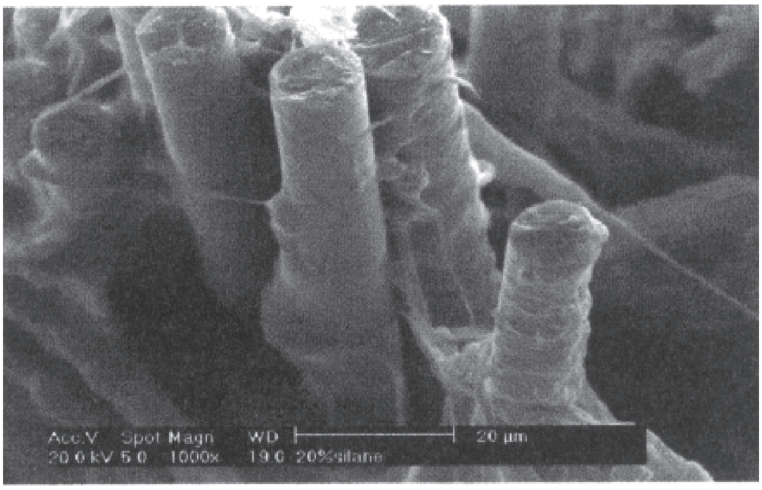

Figure 6(e) Scanning electron micrograph of tensile fracture surface of glass fiber mats reinforced TPNR composites treated with 20% silane concentration

4.0 CONCLUSIONS

In this study, the effect of silane coupling agent on the mechanical properties of TPNR reinforced by glass fiber mat has been investigated. The mechanical properties of the composite showed an improvement from 0 to 15% silane concentration. The results indicated that silane acted as curing agent, which would enhance the interfacial region between TPNR matrix and glass fiber mat by formation of cross-linking at the interface to obtain a good adhesion. However, there is no significant difference of hardness value with the increase of silane concentration. The increase of the bond strength between glass fiber mat and TPNR matrix with the increase of silane concentration is also supported by the SEM analysis.

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