Shear Strength of Single Lap Joint Aluminium-Thermoplastic Natural Rubber (Al-TPNR) Laminated Composite

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Abstract. In this work, we studied the effect of surface treatment on the aluminium surface and a coupling agent to improve adhesion between aluminium with organic polymer. Thermoplastic natural rubber (TPNR) matrix was prepared by melt blending of natural rubber (NR), liquid natural rubber (LNR) compatibilizer, linear low density polyethylene (LLDPE) and polyethylene grafted maleic anhydride (PE-g-MAH). The PE-g-MAH concentration used was varied from 0% - 25%. In addition, the aluminium surface was pre-treated with 3-glycidoxy propyl trimethoxy silane (3-GPS) to enhance the mechanical properties of laminated composite. It was found that the shear strength of single lap joint Al-TPNR laminated composite showing an increasing trend as a function of PE-g-MAH contents for the 3-GPS surface treated aluminium. Moreover, the scanning electron microscope (SEM) revealed that the strength improvement was associated with the chemical state of the compound involved.

1. Introduction

Recently, a lot of attention has been focused on the development of polymer matrix composite with metals (sandwich/laminate composite). These composites are used in a wide range of applications such as aerospace, automotive, implants, electronic, packaging, defense and medical. As compared to homogenous metal sheets, the metal-polymer laminated composite have many unique properties in terms of low density and weight, high bending strength as well as good sound, vibration and damping characteristics. [1-5].

The preparation of suitable metal-polymer laminate requires many practical considerations. It has been established that one of the most important considerations is the pretreatment process of metal surface either by mechanical, chemical, electrochemical and coupling agent [6-11,14,15]. Usually polar materials with good strength are selected as a polymer matrix. Functional groups like C=O, OH, COOH, NH₃, etc., make a polar polymer with inherent surface strength better than the non-polar polymers. The non-polar polymers can be surface modified by surface oxidizing, chemical etching,
surface grafting, flame treatment, electron beam, microwave irradiation, etc. [1,3,10,11]. Apart from these treatments, the adhesion between polymeric material with the primary metal structures also requires some attention. It is well-known that the polyethylene exhibits insufficient adhesive bond strength due to low surface energy. This property drawback has been solved by chemical, thermal, mechanical and electrical treatments. However, the dry treatment method is more suitable for industrial applications. Previous works have shown the effect of maleic anhydride coupling agent [4,10,11] by imparting polarity to a polyolefin surface that enables an improved adhesive bonding with aluminium and pretreated aluminium surface [6-8]. In the present work, we investigated the potential use of polyethylene grafted maleic anhydride (PE-g-MAH) coupling agent in the thermoplastic natural rubber (TPNR) LLDPE/NR/LNR matrix for Al-TPNR laminated composite. In the addition, the 3-GPS used as pretreatment to the surface of ground aluminium sheet in order to improve the shear strength of single lap joint aluminium-TPNR laminated composite.

2. Experimental

2.1. Material

Natural rubber (NR) was obtained from the Rubber Research Institute of Malaysia (RRIM). Liquid natural rubber (LNR) was prepared in our laboratory by photochemical oxidation of natural rubber (NR) [13]. Linear low density polyethylene (LLDPE) from Exxon Mobil Chemical Manufacturing Singapore was used. The metal used is a pure aluminium sheet with specifications; thickness 1.5 mm, serial number AA1100 (Al = 99.00%; Si & Fe = 0.05%, Mn = 0.05%; Zn = 0.10%; Cu = 0.05-0.2% and other content = 0.05%). Other materials used are polyethylene-grafted-maleic anhydride, PE-g-MAH (melting point = 105 °C; d = 0.925 g/mL) and silane coupling agent of 3-glycidoxy-propyl-trimethoxy-silane (3-GPS), [NH$_2$(CH$_2$)$_3$Si(OCH$_3$)$_3$], both are manufactured in Aldrich Chemistry USA.

2.2. Preparation of Al-TPNR laminated composite

Thermoplastic natural rubber (TPNR); LLDPE, NR, LNR (80 : 15 : 5) and PE-g-MAH were blended by using an internal mixer, ThermoHaake, at 140 °C, rotor speed 50 r.min$^{-1}$ and mixing time of 12 minutes. Various concentrations of PE-g-MAH (0%, 5%, 10%, 15%, 20% and 25%) were incorporated into the compounds. The matrix is made of thin layers using a compression molding at a temperature of 160 °C, pressure 0.5 MPa for 15 min. Aluminium sheets were cut to single lap shear tensile test, following to the standard of ASTM D 1002-72 for the sandwich structure. The aluminium sheets were boiled in distilled water for 30 min, cleaned with acetone at room temperature, and then ground with sandpaper of P800A. After that, the aluminium sheets were cleaned again with acetone at room temperature and then dried in the ambient air. Several sheets of aluminium were treated by dipping into a solution of 3-GPS 1% (in ethanol), for 5 minutes, then stirring continuously for another 30 minutes. The sample matrix was then placed between two aluminium sheets and compressed to 10 minutes under the pressure of 0.5MPa, at 160 °C temperature.

2.3. Characterization of Al-TPNR laminated composite

Tensile properties were measured using Testometric M500-50CT tester with a crosshead speed of 1 mm/min. Fracture surface morphology of single lap shear tensile samples was carried out by using LEO 1450VP scanning electron microscope (SEM). Various elements, functional groups and bonds formed on the top surface of the aluminium were investigated using X-ray photoelectron spectroscopy (XPS) AXIS Ultra DLD and spectrum 400 FTIR with ATR method analysis.
3. Result and discussion

3.1. Lap Shear Strength

The shear strength of the single lap joint of laminate composite was performed to analyze the effect of surface roughness, polymer type and metal surface treatment to the bond strength between metal and polymer (interface adhesion mechanism). It has been widely postulated that the creation of covalent bonds at the interface is sufficient for creating viable adhesive strength in adhesion-related applications [3,11,14].

Figure 1 shows the shear strength of single lap joint Al-TPNR laminated composite with TPNR plus PE-g-MAH and the coupling agent, 3-GPS, which was added as a pretreatment on the surface of the aluminium sheet. With the addition of 15% PE-g-MAH into the TPNR, the lap shear strength increased from 0.58 MPa to 5.98 MPa as compared to TPNR system only. This remarkable increment of 931% was further enhanced for the laminate composite treated with 3-GPS 1% coupling agent. The lap shear strength was further increased to 13% against the untreated laminate composite. This could be contributed by the physical interactions, such as the van der Waals interaction between TPNR and surfactants of the pretreated aluminium sheets as well as the mechanical interlocking between TPNR and surface roughness of the aluminium sheets at the interface. With the addition of grafting maleic anhydride into polyolefin and coupling agent on the aluminium surface, the increase in the lap shear strength should be ascribed to the contribution of chemical interactions at the interface [3,5,9,11,15]. The contribution includes the chemical interactions and physical strength at the interface.

3.2. XPS analysis

An XPS spectrometer of the aluminium surface after the pretreatment procedure is shown in the Figure 2(a) and 2(b) respectively. Al 2p spectra after pretreatment showed the formation of Al-OOH, Al-Si bond (Al₂SiO₅), while C 1s showed formation of CO, COC, COH and COOH on the surface of aluminum. The formation of -OH functional groups on the surface of the aluminium, resulted in physical interaction, such as the van der Waals interaction between TPNR or PE-g-MAH and surfactants (3-GPS) of the pretreated aluminium sheets at the interface. This has contributed to the interfacial adhesive strength improvement if chemical interactions at the interface existed [4,6,10,14,15].
3.3. FTIR spectroscopy analysis

Figure 3 shows FTIR spectra of LLDPE, PE-g-MAH, NR, TPNR (LLDPE/NR/LNR) and TPNR plus PE-g-MAH (LLDPE/NR/LNR/PE-g-MAH). The functional groups that are related to the chemical state of Al-TPNR laminated composite interfaces such as a C=O can be characterized in the frequency 1709 cm\(^{-1}\) (for PE-g-MAH), 1645 cm\(^{-1}\) (for system LLDPE/NR/LNR) and –OH in the frequency 3394 cm\(^{-1}\) respectively. The appearance of functional groups C=O and –OH was believed to have formed during mixing as a result of material oxidation. These functional groups are important in the physical and chemical interactions in the bonding interface of Al-TPNR laminated composite [3,4,10].

![Figure 2a. XPS spectra Al 2p of on the aluminium surface with 3-GPS, separated polymer surface Al-TPNR laminated composite.](image)

![Figure 2b. XPS spectra C 1s of on the aluminium surface with 3-GPS, separated polymer surface Al-TPNR laminated composite](image)

![Figure 3. FTIR spectra for LLDPE, PEgMAH, NR, LLDPE/NR/LNR and LLDPE/NR/LNR/PEgMAH.](image)
3.4. SEM analysis

Figure 4 (a, b) shows the SEM micrographs of the lap shear fractured aluminium surfaces without PE-g-MAH in TPNR matrix and coupling agent, 3-GPS. It can be seen in Figure 4 (a) that almost all aluminium surfaces are clearly visible and almost no inherent TPNR. In contrast, when the PE-g-MAH was added and aluminium surfaces pretreated with 3-GPS, it appears the fracture surface of aluminum remains as a strong matrix inherent as shown in Figure 4 (b). Chen et al [3] reported that pretreatment aluminum surface with the addition of coupling agent and maleic anhydride grafted into the plastic has enhanced the adhesion strength between polymer matrices with metal; hence an improved composite laminate could be obtained [10,15].

![Figure 4(a). SEM images of lap shear fractured surface of the adhering aluminum sheet without 3-GPS and PE-g-MAH.](image)

![Figure 4(b). SEM images of lap shear fractured surface of adhered aluminium sheet with 3-GPS and PE-g-MAH 1 wt% added in TPNR matrix.](image)

4. Conclusions

The shear strength of single lap joint Al-TPNR laminated composite increased by 931% when the PE-g-MAH was added at 15% into the TPNR. With the 3-GPS 1% coupling agent on the treated aluminium surface, the lap shear strength was further increased by another 13% as compared to the untreated laminate composite. These phenomena could be associated with the chemical interaction between the AlOOH, COOH, CO, COC, COH and Al-Si (Al₂SiO₅) as confirm by the XPS, FTIR and SEM analysis.

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