JOINING AND INTERFACIAL PROPERTIES OF ALUMINUM/GLASS FIBER REINFORCED POLYPROPYLENE SANDWICH COMPOSITES

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ABSTRACT

JOINING AND INTERFACIAL PROPERTIES OF ALUMINUM/GLASS FIBER REINFORCED POLYPROPYLENE SANDWICH COMPOSITES

The joining of separate components using a suitable technique is a critical step in the manufacture of composite structures. For good property performance of aluminum/glass fiber reinforced polypropylene (Al/GFPP) laminates, one of the most important problems is to obtain good adhesive bond strength.

In the present study, Al/GFPP laminates have been manufactured with various surface pretreatment techniques. Adhesion at the composite/metal interface has been achieved by surface pretreatment of Al with amino based silane coupling agent, incorporation of polyolefin based adhesive film and modification with PP based film containing 20 wt. % a maleic anhydride modified polypropylene (PP-g-MA). The mechanical properties shear, peel and bending strength of the adhesively bonded Al/GFPP laminates were investigated to evaluate the effects of those various surface treatments. In addition, peel strengths of Al foam/GFPP laminates with various surface treatments were measured. The fracture surfaces have been examined by scanning electron microscope (SEM).

Results showed that the adhesion of the laminated Al/GFPP systems were improved by treatment of aluminum surfaces with amino-based silane coupling agent. Based on peel and bending strength results, Al/GFPP laminates with incorporation of polyolefin based adhesive films exhibited significant increase on the adhesive behaviour. Modification of Al/GFPP interfaces with PP-g-MA layer leads to highest improvement on the adhesion properties.

ÖZET

ALUMİNYUM/CAM ELYAF İLE TAKVİYE EDİLMİŞ POLİPROPİLEN SANDVİÇ KOMPOZİTLERİN BİRLEŞTİRİLMESİ VE ARAYÜZEY ÖZELLİKLERİ

Farklı parçaları uygun yöntemlerle birbirine bağlamak kompozit yapı üretiminde kritik bir adımdır. Aluminyum/cam elyaf takviyeli polipropilen tabakalı kompozitlerin (Al/CEPP) özelliklerinde gelişmiş performans elde etmekte karşılaşılan en önemli problem iyi bağlanma mukavemetinin sağlanmasıdır.

Bu çalışmada, Al/CEPP tabakalı yapılar çeşitli yüzey önişleme teknikleri kullanılarak üretilmiştir. Kompozit/metal arayüzeyinideki bağlanma, aluminyumun amino bazlı silane bağlayıcı ajan ile önişlenmesi, poliolefin bazlı yapıştırıcı film eklenmesi ve Al yüzeyinin ağırlıkça % 20 maleik anhidrid polipropilen (PP-g-MA) içeren polipropilen bazlı film ile modifikasyonu ile elde edilmiştir. Bu çeşitli yüzey önişlemelerin etkilerini değerlendirmek için bağlanmış Al/CEPP tabakalı yapıların mekanik özellikleri (kayma, ayrılma ve eğme mukavemetleri) incelenmiştir. Ayrıca farklı yüzey önişleme teknikleri kullanılarak modifiye edilen Al köpük/CEPP tabakalı yapıların ayrılma mukavemetleri ölçülmüştür. Ayrılma testinden sonraki kırık yüzeyler taramalı elektron mikroskobu (SEM) ile incelenmiştir. Çeşitli yüzey önişlemeleri ile elde edilen Al/CEPP tabakalı yapıların dayanıklılığı, yapışma özelliklerinin tabakalı yapıların yaşlandırılması üzerindeki etkilerini elde etmek için değerlendirilmiştir.

Sonuçlar göstermiştir ki, Al/CEPP tabakalı sistemlerin bağlanması aluminyum yüzeylerinin amino bazlı silan bağlayıcı ajanı ile yüzey önişlemine tabi tutulmasıyla gelişmiştir. Ayrılma ve eğme mukavemetleri sonucuna göre, poliolefin bazlı yapıştırıcı film eklenmesi ile elde edilen Al/CEPP tabakalı yapılar yapışma davranışlarında önemli ölçüde artış sergilemiştir. Al/CEPP arayüzeylerinin PP-g-MA tabakalarıyla modifikasyonu ile bağlanma özelliklerinde en iyi gelişme elde edildiğini göstermiştir.

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CHAPTER 1

INTRODUCTION

Metal/polymer laminated composite laminates, have been used in a wide variety of applications in electronics, automotive, defence and aerospace industries because they tailor the overall mechanical properties of the laminated structure based on the properties of the constituents. For instance, in order to increase automobile and aircraft efficiency and to reduce fuel consumption and contaminant emissions, a weight reduction coupled with an improvement of the safety performance of the candidate materials must be achieved (Reyes and Kang 2007). For this particular reason, there have been continuous efforts to make automotive body parts from aluminum alloy sheets instead of steel sheets. In fact, aluminum alloy sheets have already been used for the body panels of super luxury vehicles. The polymer may be used for significant weight savings over the corresponding metal components but without any loss of strength and stiffness, specific mechanical properties such as impact response, thermal insulation property and acoustic damping, corrosion protection, etc. (Chen, et al. 2007; Kim and Yu 1997).

In recent years, metal–plastic laminates and sandwich sheets have been developed in order to considerably reduce the weight of vehicles and improve the sound-deadening properties of the material. To date, the focus of research into composite/metal laminates has been on thermoset resins, namely epoxy, and aluminum. Fiber/metal laminates (FML) such as GLARE® and ARALL®, which are laminates of aluminum and glass or aramid reinforced epoxy respectively, have been under development for the aerospace industry since the early 1980s. These materials have been found to exhibit excellent fatigue resistance, impact resistance and damage tolerance, and are now finding significant application in commercial aircrafts. However, such thermosetting-based composites are often brittle and, for optimum consolidation of parts made from prepreg, elevated processing temperature and pressure are required for a prolonged period (Weager and Rudd 1999).

Thermoplastic-based laminates have received comparatively little attention, however, the fast production times, high recyclability and low volatiles offered by thermoplastics make them attractive. Other benefits are likely to include: (i) the possibility to reform and reshape components following manufacture (ii) ease of repair (iii) all round excellent energy-absorbing characteristics and (iv) a high resistance to localised impact loading (Reyes and Cantwell 2000).

Polypropylene (PP) has excellently balanced physical and mechanical properties. Glass fiber-reinforced polypropylene (GFPP) is of particular interest due to its relatively low cost. In recent years, thermoplastic polymer/metal-based components and laminated composites, such as aluminum/thermoplastic/aluminum-laminated sheets and steel/PP or nylon/steel-laminated sheets for weight reduction of car body panels, have received researchers' attention. In addition, steel or aluminum sheet/fiber reinforced thermoplastic polymer-laminated sheets have also gained attention. However, in order to apply Al/PP/Al sandwich sheets for automotive body panels, many requirements have to be met such as the proper combination of strength, flexural rigidity and formability, dent and corrosion resistance, joinability, recyclability, etc. (Kim, et al. 2003). A few examples of thermoplastic/metal hybrids can be found in the literature. Hylite is an aluminum/ polypropylene/aluminum sandwich sheet developed by Corus for use in automotive bonnets. A weight saving of 65 % has been reported for a Hylite® part over a steel part of equal stiffness, although costs remain prohibitive (Burchitz, et al. 2005).

The adoption of composite components into predominantly metal body structures presents a number of problems for automotive manufacturers. These include the difficulties of joining and surface quality. For good property performance of aluminum sheet/PP laminate composites, one of the important problems is to obtain good adhesive bond strength, strongly enough to withstand stresses and strains that might appear in the forming process as deep drawing and bending and in services, between them should be obtained. 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 (Bistac, et al. 1998, Chen, et al. 2007).

However PP, being a polyolefin, is generally hydrophobic and shows low-surface free energy (29 mN m^{-1}) presenting serious adhesion difficulties bonding to other materials, even to polar materials, which has so far limited the widespread use of PP and other polyolefins under mass production conditions where joining is necessary

(Roover, et al. 1995, Zhou, et al. 2000). For this reason, a modification of the surface is necessary to produce well-adhering compounds. As the use of both aluminum and thermoplastics continues to increase, there will be an ever growing need to efficiently join sub-components during manufacturing and assembly. Whilst much has been written on the subject of adhesive bonding, knowledge is still inadequate, and the engineering tools available for the through-life management of adhesively bonded structure are primitive (Baker, et al. 2002).

Many pretreatments are available ranging from a simple solvent wipe to the use of a series of complex chemical processes. Different groups of materials, i.e. metals, inorganic glasses, plastics, elastomers, etc., tend to have their own specific pretreatments. However, some pretreatments are effective with different groups of materials, for example, silanes can greatly enhance the performance of joints involving either metals or inorganic glasses. With regard to the PP composites, the interphase may be tailored with a silane coupling agent, a bonding agent or an additive agent such as maleic anhydride into matrix PP (Hamada, et al. 2000).

Demjen et al. (1999) focused on the mechanism of interaction between the silane coupling agents and the polypropylene matrix. They showed that aminofunctional silanes bond strongly to the surface of the $CaCO_3$ filler. Chen et al. (2007) found that pretreatment of the aluminum surfaces by amino based silane leads to an increase in the lap shear strength.

Maleic-anhydride-modified PP (PP-g-MA) is the polymer, that received great interest for many applications such as anticorrosive coatings for metal pipes and containers, metal-plastic laminates for structural use, multilayer sheets of paper for chemical and food packaging, and polymer blends.

Chen et al. (2007) modified PP by the addition of 5–30 wt. % amount of PP-g-MA. The lap shear strengths were improved as compared to unmodified ones. Reyes and Cantwell (2000) achieved adhesion between Plytron (Borealis, Norway), a unidirectional glass-fiber reinforced polypropylene, and 2024-T0 aluminum alloy by applying an amorphous chromate treatment to the aluminum and incorporating PP-g-MA at the interface. Compston et al. (2001) applied an amorphous chromate treatment to the aluminum and incorporated a layer of PP-g-MA at the E-glass fiber/polypropylene composite-aluminum interface in order to provide optimum adhesion between the layers.

The objective of this study is to develop fiber/metal laminates based on glass fiber reinforced polypropylene composites and aluminum which are exposed to different pre-treatment techniques. Investigation of the various surface treatments on the adhesive properties of the fiber/metal laminates is also the aim of the present work.

CHAPTER 2

LAYERED COMPOSITES

2.1. Metal/Polymer Laminates

During last few decades, many scientists have been aiming their efforts to develop new materials, which would retain the low weight and good mechanical properties of aluminum alloys. Metal-polymer laminated composite, one of the unique combination of these two kinds of different materials used to achieve improved quality of the products, has been used in a wide variety of applications in electronics, automotive, and aerospace industries, etc. (Gresham, et al. 2006). Metal–composite systems consist of alternating layers of metal and fibre-reinforced polymer (FRP) composites, bonded by an adhesive layer as shown in Figure 2.1. They combine both the good characteristics of metals such as ductility, impact and damage tolerances with the benefits of fiber composite materials such as high specific strength, high specific stiffness and good corrosion and fatigue resistance. They can be a good choice for main aircraft structures, for example in lower and upper wings as well as in the fuselage and tail sections (Khalili, et al. 2005).
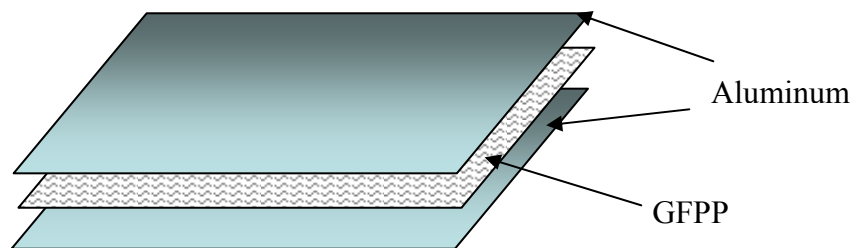
Figure 2.1. Schematic of sandwich lamination

The first generation metal-polymer laminates, for aerospace applications, were based on composites with epoxy thermosetting polymer matrices, which offer higher strength and stiffness and superior high temperature performance compared to other

polymer matrices. However, such thermosetting-based composites are often brittle and, for optimum consolidation of parts made from prepreg, elevated processing temperature and pressure are required for a prolonged period. Recent attention has focused on thermoplastic-based composites since they offer a number of advantages such as rapid manufacturing and recyclability. In comparison, metal-polymer laminates with thermoplastic-based composites offer improved toughness and has the potential for short process cycle times. This can lead to rapid, low-cost production of structural components. Here, the use of a thermoplastic-based composite ensures the production of aerospace and automotive panels and components that can be molded, bonded to a metal substrate and shaped in a simple oneshot manufacturing operation. This procedure clearly offers an attractive option for reducing both the cycle time and associated manufacturing costs. In addition, the high recyclability and low volatiles offered by thermoplastics are key factors for vehicle manufacturers; the low density and low cost of polypropylene is particularly attractive. Although PP is difficult to join, glass fiber-reinforced polypropylene is of particular interest due to its relatively low cost (Reyes and Kang 2007).

2.2. Adhesive Joining Methods

A critical step in the manufacture of composite structures is the joining of seperate components using a suitable technique. The application of compounds depends strongly on the adhesion between the parts. Traditional joining methods include mechanical fastening and thermosetting adhesives. Alternatively, thermoplastic composite components have the ability to be welded. Also known as thermoplastic fusion bonding, welding has been shown to be an effective technique for joining and repairing thermoplastic and thermoplastic composite materials. There are several methods of fusion bonding, which are distinguished by the method of heat generation: infrared, hot plate, ultrasonic, resistance and induction (McKnight, et al. 1993). These methods are generally capable of joining thermoplastics to themselves and other thermoplastics, and in certain cases they may also be used to weld thermoplastics to nonplastic substrates (Adams 2005).

Polypropylene (PP) and other polyolefins are increasingly being used for industrial automotive applications due to their advantageous properties and ability to be readily recycled. However, PP is generally hydrophobic and shows low-surface free energy resulting in very poor bondability to other materials, even to polar materials, which has so far limited the widespread use of PP and other polyolefins under mass production conditions where joining is necessary (Chen, et al. 2007). Effective surface modification techniques are being sought to overcome these shortcomings, so enabling a durable and strong joint to be manufactured (Green, et al. 2002).

In plastics bonding, surface preparation is aimed at increasing the surface polarity, improving surface wettability, and creating sites for adhesive bonding (Ebnesajjad 2006).

Many pretreatments are available ranging from a simple solvent wipe to the use of a series of complex chemical processes. A pretreatment can act by removing potential weak boundary layers, WBLs, by altering the substrate topography, by modifying the chemistry of the substrate surface or by a combination of these mechanisms (Ebnesajjad 2006).

Treatments may be divided into physical and chemical methods. Physical treatments include solvent degreasing and grit blasting and may remove cohesively weak layers from a substrate, i.e. potential WBLs, and they may also modify topography. Chemical treatments such as flame treatment of plastics (Green, et al. 2002) and anodising procedures for metals, by definition cause chemical modification to the surfaces involved (Baker, et al. 2002).

Different groups of materials, i.e. metals, inorganic glasses, plastics, elastomers, etc., tend to have their own specific pretreatments. However, some pretreatments are effective with different groups of materials, for example, silanes can greatly enhance the performance of joints involving either metals or inorganic glasses (Adams 2005).

Pretreatments for metals have been the subject of many research. This is especially true in the case of aluminum where particular emphasis has been placed on aerospace applications. There is of course great interest in commercial and military aircraft and much research has been carried out by manufacturers of aircraft, defence establishments, adhesive manufacturers, suppliers of pretreatment materials and academic institutions. Etching of aluminum with chromic acid etching (CAE) was found to give greatly enhanced performance compared to physical methods. However, chromic acid anodising (CAA) or phosphoric acid anodising (PAA) was generally

found to be even more effective especially in relation to the durability in wet conditions (McKnight, et al. 1993).

Chromic acid is highly toxic and corrosive; further, anodising is a complex multistage process. Much effort has been made to find safer and simpler pretreatments. For instance the use of silanes is an alternative. Much effort is being made to optimise the use of silane primers as a viable alternative to CAA and PAA treatments. It is now generally agreed that topography and oxide stability have a critical effect on resultant joint performance (Adams 2005).

The surfaces can be modified by a number of pre-treatment techniques, including mechanical roughening, plasma treatment or by generating intermediate layers of chemically synthesized polythiophene, plasma polymerized acrylic acid (Dayss, et al. 1999), chemical etching as chromic acid etching, surface grafting, flame treatment (Pijpers and Meier 2001), electron beam and microwave irradiation, plasma discharge as corona discharge and glow discharge (Green, et al. 2002), fluorination, vacuum plasma, atmospheric plasma, infrared laser, silver electrolysis etc. The modification processes related to adhesion are aimed mainly at creating polar groups on surface of polymers, thus increasing the surface free energy values and improving adhesive properties of the polymeric materials (Chen, et al. 2007).

With regard to the PP composites, it can be said that the interphase control can be conducted with a silane coupling agent and a binding agent or an additive agent such as maleic anhydride into matrix PP (Hamada, et al. 2000).

2.2.1. Chemical Treatment with Silane Coupling Agents

The chemical bonding theory of adhesion invokes the formation of covalent, ionic or hydrogen bonds or Lewis acid-base interactions across the interface. Adhesion promoters or coupling agents are a group of specialty bifunctional compounds that can react chemically with the substrate. Adhesion promoters can be applied directly to the substrate, or they can be mixed with the adhesive itself. When mixed with the adhesive, the coupling agent is capable of migrating to the interface and reacting with the substrate surface as the adhesive cures. When applied directly to the substrate, adhesion

promoters are applied in a very thin coating that ideally is only one molecular layer thick (Petrie 2000).

Coupling agents add a new, usually organic layer at the interface as shown in Figure 2.2. The new layer is usually bifunctional and bonds well to both the substrate (such as metal) and the adhesive (such as polymeric material). The new layer is very thin so that it provides improved interfacial bonding characteristics, yet it is not thick enough so that its bulk properties significantly affect the overall properties of the bond (Baker, et al. 2002).
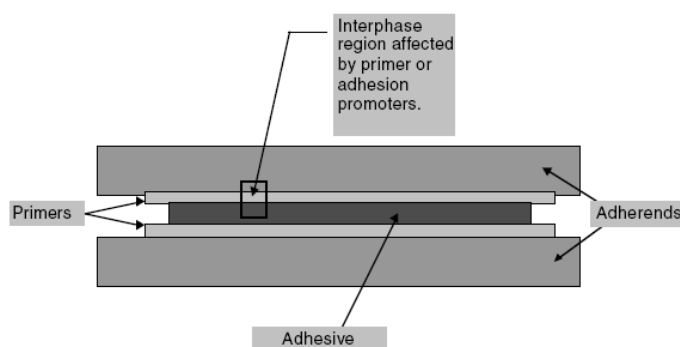
Figure 2.2. Coupling agents provide a stronger interphase region having improved adhesion and permanence (Source: Baker, et al. 2002)

Coupling agents are strongly adsorbed onto the surface of the substrate. The adsorption may be so strong that instead of merely being physical adsorption, it has the nature of a chemical bond. Such adsorption is referred to as chemisorption to distinguish it from reversible physical adsorption. Usually chemical bonds are formed between the coupling agents and the adhesive, and between the coupling agents and the substrate surface (Baker, et al. 2002).

Silanes are the most common commercial adhesion promoters. They are commonly used to enhance adhesion between polymeric and inorganic materials. Coupling agents can be applied by either incorporating them directly into the adhesive formulation or by applying them to a substrate (Petrie 2000).

Silane coupling agents are generally considered to chemically react with both substrate and adhesive, so forming a system of covalent bonds across the interface, which is both strong and durable. They usually consist of molecules with short organic chains having different chemical composition on either end of the chain. As shown in Figure 2.3, on one end is an organofunctional group that is particularly compatible with

the given adhesive material. At the other end of the chain is an inorganic functionality that is especially compatible with a given substrate. The adhesion promoter, therefore, acts as a chemical bridge between the adhesive and the substrate (Petrie 2000). For instance, the Si-O bond is formed when silane coupling agents are used on glass (Demjen, et al. 1999).

$$X - Si(OR)_3$$

$$X \sim Si(OR)_3 + 3H_2O \longrightarrow X \sim Si(OH)_3 + 3RO$$
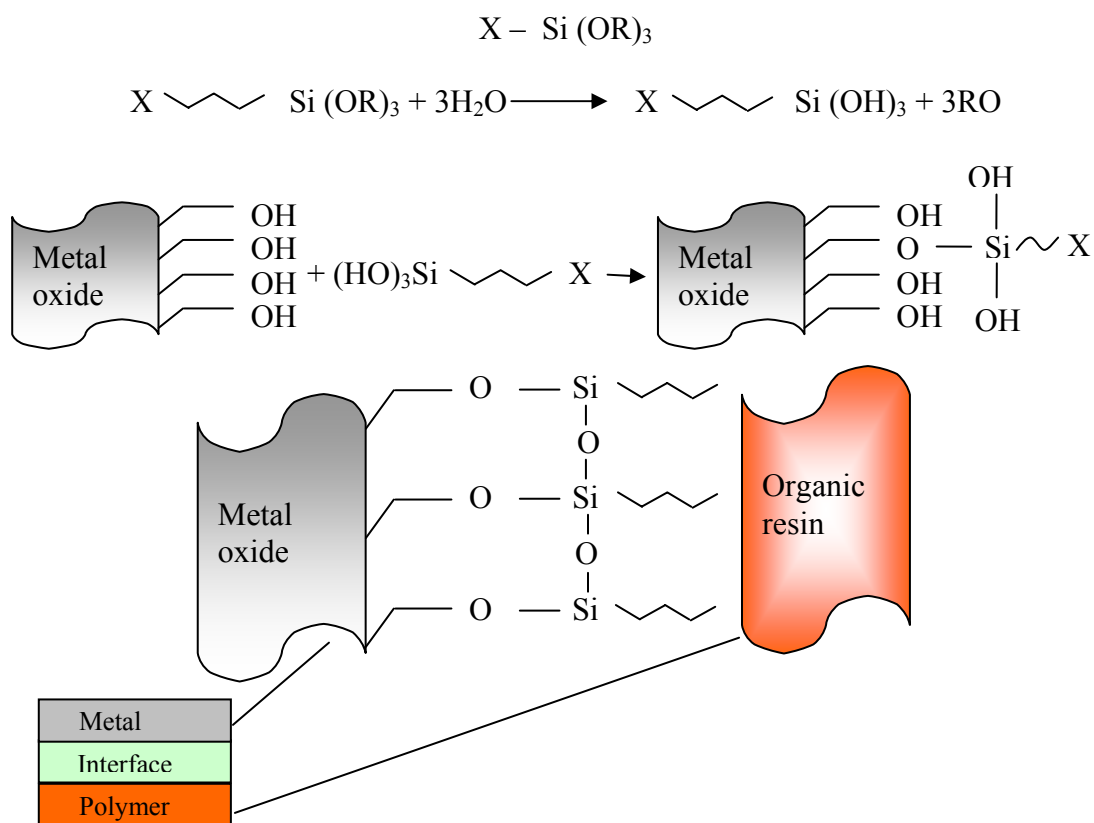
Figure 2.3. Chemical structure of an organosilane, organosilane hydrolysis and condensation reaction mechanisms

In general terms, a silane coupling agent can be represented by $X-Si(OR)_3$, where X units represent a range of organofunctional radicals that are selected to react with or adhere to the resin in the adhesive or the organic medium, Si is silicon and the OR units are hydrolyzable alkoxy groups such as methoxy (OCH_3), ethoxy (OC_2H_5) and acetoxy ($OCOCH_3$) that provide adhesion to the inorganic or substrate surface (Han, et al. 1981). Silane coupling agents are commonly used between the adhesive and the adherend, between resin matrix and reinforcing fibers in composites, between resin matrix and mineral fillers in plastic compounds and also between the components of laminated structures. The resulting interface provides;

1) A chemical bridge between the surface and organic polymer or between organic polymers

2) A barrier to prevent moisture penetration to the interface

3) Transfer of stress from the resin to the substrate or inorganic filler component thereby improving joint strength or bulk properties

4) Effective dispersion of fillers and reduction in the apparent viscosity of the system (Petrie 2000).

They are normally applied to adherends from dilute solution in water or ethanol-water (1-2% by volume) and left to drain and dry. They can also be added to adhesives (Cognard 2006). Silane coupling agents react with water in aqueous solutions to form hydrolyzed silanes, which react with the surface of the inorganic substrate. Hydrolysis of the alkoxy groups occurs with the formation of silanol groups. The silanol groups in the silane are able to react with a metal surface to form a primary bond (Si±O±Si)). The purpose of the coupling agent is to enhance the effectiveness of the hydroxyl (OH) terminations on the metal oxide in linking with the adhesive. The X groups in the silane may be able to react with a chemical group in the adhesive or alternatively chain entanglement between the polysiloxane and adhesive may occur; both of these mechanisms lead to a relatively stable bonding. The hydrolysed silane thus acts as a bridge or coupling agent between the metal and the polymer. This is true whether the polymer is an adhesive, or the matrix of a composite. This process is shown in Figure 2.3 (Adams 2005).

There are a number of silane adhesion promoters available, and they differ from each other in the degree of their reactivity. Silanes may be produced with amine, epoxy, mercaptan, and other functionalities. Structures of some commercially available silanes are shown Table 2.1. The -R groups in the 3-aminopropyltriethoxysilane (APES) and N-2-aminoethyl-aminopropyltrimethoxysilane (AAMS) contain amines, which would make them reactive with epoxide adhesives or liquid resins. As 3-glycidoxypropyltrimethoxysilane (GPMS) contains epoxide groups, it would react with amine groups in adhesives or resins. The carbon carbon double bonds in 3-methacrylpropyltrimethoxysilane (MPMS) would copolymerise with styrene and unsaturated polyester in liquid resins, by a free radical mechanism (Cognard 2006).

Thermoplastic polymers, especially the apolar polyolefins, are inactive, since their polymer chain does not contain any reactive groups. Reactive coupling is not expected in such systems. Trialkoxy functional silane coupling agents containing

reactive organofunctional groups have been successfully applied for the treatment of glass fibers embedded in thermoset resin matrices. Surface treatment of fillers and reinforcements is a wellknown way to modify the interfacial interaction in polymer composites. In such systems, the coupling agent can react with the active surface of the fiber and the reactive groups of the resin. Because of the high efficiency of silanes in advanced composites, they are often also used in experiments in polyolefins filled with inorganic materials like mica, $CaCO_3$ or other mineral fillers (Demjen, et al. 1999).

Table 2.1. Structures of some commercially available silane coupling agents

Abbr.	Formula
APES	$NH_2-CH_2-CH_2-CH_2-Si(O-CH_2-CH_3)_3$ 3-Aminopropyltriethoxysilane
AAMS	$NH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(OCH_3)_3$ N-(2-aminoethyl)-aminopropyltrimethoxysilane
GPMS	$\overset{\displaystyle O}{\overset{\diagup \diagdown}{CH_2-CH-CH_2-O-CH_2-CH_2-CH_2-Si(OCH_3)_3}}$ 3-Glycidoxypropyltrimethoxysilane
MPMS	$CH_2=CH-COO-CH_2-CH_2-CH_2-Si(OCH_3)_3$ $\mid$ CH_3 3-Methacrylpropyltrimethoxysilane

Demjen et al. (1999) focused on the mechanism of interaction between the silane coupling agents and the polypropylene matrix. They reported the results of model experiments, analysed the possible reactions and developed a tentative explanation to explain reactive coupling in an apparently inert system. Silane coupling agents used in the model reactions are listed in Table 2.2. They showed that aminofunctional silanes bond strongly to the surface of the filler, aminofunctional silane coupling agents adhere strongly to the surface of $CaCO_3$ and form a polysiloxane layer probably due to the catalytic effect of the amino group in the polycondensation process. It is concluded that,

N-4-vinylbenzyl-N9-3-trimethoxysilylpropyl-ethylenediamine hydrochloride (CVBS), aminosilane coupling agent, reacts with the carboxyl groups of PP, forming tertiary amide groups. Reactions are also fast in this case, they are completed during the homogenization of the composite, leading to the reactive coupling effect observed.

Table 2.2. Silane coupling agents used in the model reactions
(Source: Demjen, et al. 1999)

Abbr.	Formula	Grade	Producer
MPMS	$CH_2{=}C{-}CO{-}O{-}CH_2{-}CH_2{-}CH_2{-}Si{+}O{-}CH_3)_3$ $\quad\quad\mid$ $\quad\quad CH_3$ (3-methacryloxypropyl)trimethoxysilane	GF31	Wacker
CVBS	$CH_2{=}CH{-}\bigcirc{-}CH_2{-}NH{+}(CH_2)_2{-}NH{-}(CH_2)_3{-}Si{+}O{-}CH_3)_3$ HCl N-(4-vinylbenzyl)-N'-(3-trimethoxysilylpropylethyl)enediamine, hydrochloride	Z6032	Dow Corning
APES	$NH_2{-}CH_2{-}CH_2{-}CH_2{-}Si{+}O{-}CH_2{-}CH_3)_3$ (3-aminopropyl)triethoxysilane	GF93	Wacker

Lee and Jang (1997) investigated the effect of APES silane coupling agent on the mechanical and impact properties of short-glass-fiber-mat reinforced PP composites. The flexural strength and the flexural modulus of the composites were increased by treating the fiber surfaces with this silane coupling agent.

The reactive coupling effect of two aminofunctional silanes APES and CVBS silane was demonstrated in $PP/CaCO_3$ composites, resulting in enhanced tensile strength and decreased deformability compared to the non-treated system (Demjen and Pukanszky 1997, Demjen, et al. 1998). Analysis of the interaction between the silane coupling agents and $CaCO_3$ showed that aminofunctional silanes adhere to the surface of the filler much stronger than other silane coupling agents (Demjen, et al. 1997). Dissolution experiments proved that the adhesion between subsequent silane layers is as strong as the adhesion between the surface and the first layer, while in the absence of amino group, the silane coupling agents could easily be dissolved from the surface of the filler (Demjen, et al. 1999).

Chen et al. (2007) showed the effect of the pretreatment of the aluminum surfaces by APES silane solution. As seen in Figure 2.4, it was found that pretreatment of the aluminum surfaces by APES silane leads to an increase in the lap shear strength.

It should be noted that in viewpoints of the durability of the adhesive bonded interface under wet and water circumstances it is preferable to having aluminum sheets being pretreated by silane coupling agent prior to adhesive bonding.
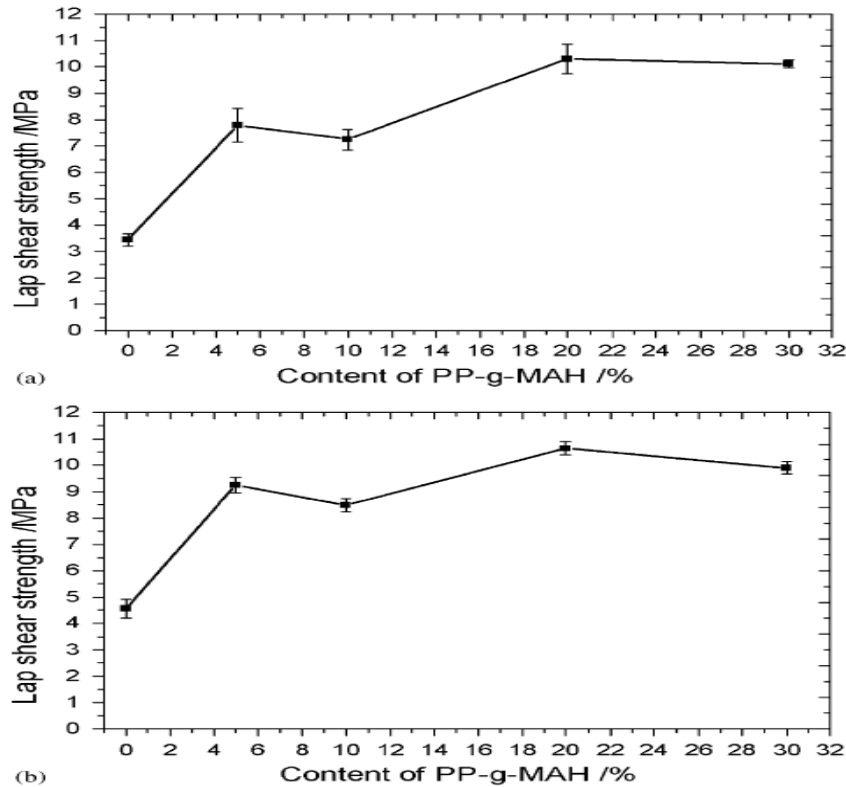
Figure 2.4. Effect of the PP-g-MA content on lap shear strength: (a) without pretreatment by APES silane solution, (b) with pretreatment by 1% APES silane solution (Source: Chen, et al. 2007)

Tanoğlu et al. (1998) employed silane coupling agents in order to improve the adhesion between vinyl–ester and alumina. Shear test by compression molding was used to study dry and wet adhesion. The results showed that the adhesion durability of the sandwiched alumina/vinyl ester systems were significantly improved by the modification of the alumina surfaces by using cationic styrylamine (CVBS) silanes abbreviated with Z-6032. The shear strength of the silane-treated and untreated control for dry as well as wet conditions is presented in Figure 2.5.

Mcknight et al. (1993) performed 3-glycidoxypropyltrimethoxy (GPMS) silane treatment on aluminum in order to provide durability in aluminum-polypropylene joints. But, GPMS did not enhance the bond between aluminum and PP, due to the lack of reactivity and compatibility between PP and epoxy based silane.
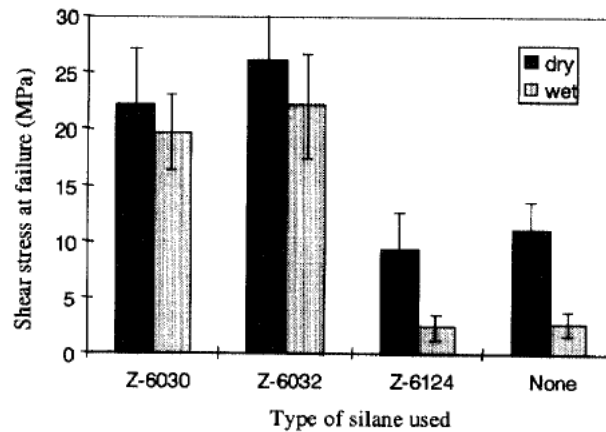
Figure 2.5. Improvements in shear strength of the silane-treated specimens under dry and wet conditions (Source: Tanoglu, et al. 1998)

Briskham and Smith (2000) produced polypropylene composite-to-aluminum fusion bonded joints by using a range of different aluminum pretreatments. The range of pretreatments listed in Table 2.3 were employed on the aluminum substrates. According to the results as seen in Figure 2.6, aminosilane pretreatment performed good results.
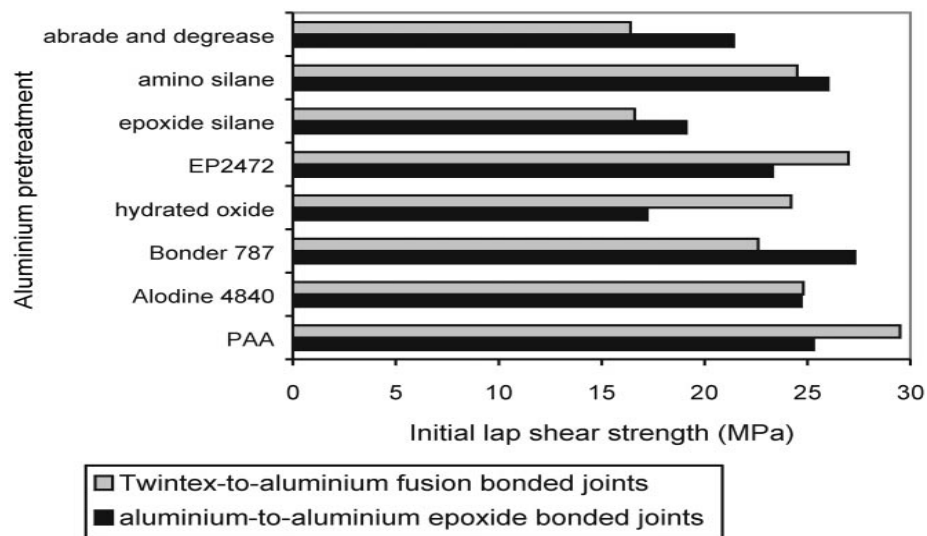
Figure 2.6. Improvements in shear strength of the silane-treated specimens
(Source: Briskham and Smith 2000)

Lawcock et al. (1997) investigated the effect of adhesion between the aluminum and fiber/epoxy prepreg on the mechanical property profile. The results with GPMS silane indicate an increase in interfacial fracture toughness up to seven times for the specimens with stronger bonding as compared with those with poor bonding.

Table 2.3. Description of the aluminum pretreatments

Pretreatments	Explanation
PAA	Phosphoric acid anodise, conducted to Boeing spec. BAC 5555
Alodine 4840	Titanium/zirconium-based conversion coating with a polymeric constituent
EP2472	Zirconium-based conversion coating with a polymeric constituent
Hydrated oxide	Titanium/zirconium-based conversion coating with an organic constituent
Bonder 787	De-oxidised aluminum hydrated in boiling distilled water
Amino silane primer	1% amino silane in an IPA solvent solution
Epoxide silane primer	1% epoxide silane in an IPAsolvent solution
Abrade and degrease	IPA degrease and Scotchbrite^{TM} abrade

Aboudzadeh et al. (2007) investigated the effect of epoxy (GPMS) and amino (APES) based silane treatments on the surface characteristics of flame-treated PP individually. By silane-based treatment, adhesion strength of flame-treated PP surfaces to acrylic lacquers significantly increased, which is due to changes in surface free energy, morphology and generation of functional groups on the PP surface. Besides, the results showed that the effect of epoxy silane in increasing adhesion strength of flame-treated PP surfaces was higher than the aminosilane.

Zhou et al. (2008) functionalized multi-wall carbon nanotubes (MWCNTs) with a MPMS coupling agent. The results showed that the PP/MPMS functionalized MWCNTs composite has higher tensile strength than the PP/raw MWCNTs composite.

Arencon et al. (2007) prepared ductile glass microsphere-filled polypropylene (PP)-matrix composites containing 50% by weight of glass beads. Glass beads were silane-treated with 3-mercaptopropiltrimetoxy silane and N-(2-aminoetil)-3-aminopropil trimetoxy silane. It was seen that in glass bead-filled samples, aminosilane (Z-6020) reduced the fracture toughness if compared with untreated and mercaptosilane-treated glass bead composites. This effect was related to a slightly enhanced interfacial adhesion promoted by the aminosilane. Liu ve Kontopolou (2006)

showed that trimethoxyoctylsilane silane-modified nanosilica dispersed more efficiently in the polypropylene matrix, giving rise to improved impact properties of the thermoplastic olefin blend based (TPO) composites, compared to the unmodified filler .

Diez-Gutierrez et al. (1999) used a mixture of vinytrimethoxy silane and gamma-methacryloxypropyltrimethoxy silane (1:3 by volume) containing 1% dicumyl peroxide for surface treatment of the mineral to study the eventual improvements obtained in the composite properties. The adhesion between the polymer and the talc was improved when the talc is treated with silanes as seen in Figure 2.7. The treated and untreated talc act as nucleating agents for the PP matrix, the effect of the treated talc was found to be more intense. Besides, it was concluded that PP–talc composites with silane does not have an effect on the talc crystals orientation.
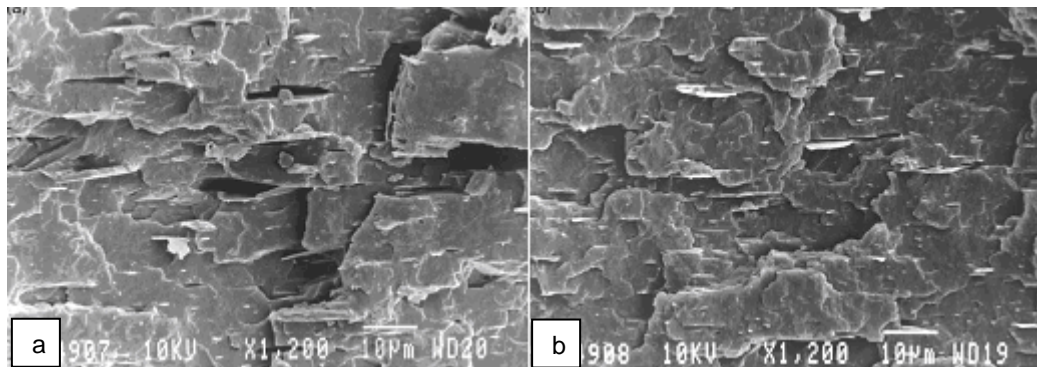
Figure 2.7. SEM images of PP–talc composites a) with and b) without silane treatment of the talc (Source: Diez-Gutierrez, et al. 1999)

2.2.2. Maleic Anhydrid Grafted Polypropylene

Maleic-anhydride-modified polyolefins are the most important class of functionalized polyolefins in current commercial applications. Due to the unique combination of the low cost of the MA reagent and functionalization process and good processibility, they are the popular choice of material for improving the compatibility, adhesion, and paintability of polyolefins. Among them, maleic-anhydride-modified PP (PP-g-MA) is the most investigated polymer, and one which has found applications in many commercial products like GFPP, anticorrosive coatings for metal pipes and containers, metal-plastic laminates for structural use, multilayer sheets of paper for

chemical and food packaging, and polymer blends (Chung 2002). The anhydride group is a very reactive and efficient coupling agent with glass fibers, fillers, and functional polymers (such as polyamides, etc.)

Maleic anhydride-functionalized polypropylene is of considerable importance for application as a copolymer precursor in polymer blends, as an adhesion promoter with glass or carbon fibers, and even as a processing aid for recycling of plastics waste. With these three domains, MAH received considerable attention in recent years (Roover, et al. 1995).

MAH is one of the most commonly used polar monomer for polyolefin functionalization, possessing a high reactivity of the anhydride group. Through reactive extrusion process, etc., polar monomers can be introduced onto the polymer chains (Shi, et al. 2001). MAH-grafted isotactic PP has been widely used as a compatibilizing agent in the composites of PP and other fillers as well as in immiscible polymer blends for improving the interaction between polymer and fillers (Roover, et al. 1995, Zhou, et al. 2000). It is assumed that chemical bonds would be formed between the introduced polar monomers and surfactants of the pretreated sheet in addition to physical adsorption. Under this case, the adhesive strength will be promoted greatly (Chen, et al. 2007).

The interaction mechanisms for interfacial adhesion between MAH-grafted PP (PP-g-MA) and Al surface is shown in Figure 2.8. Distribution of PP molecules and PP-g-MA on the Al surface is schematically illustrated in Figure 2.9. Chen et al. (2007) modified PP by adding a small proportion of functional monomer grafted PP, having the same molecular structure as PP except for the functional monomer being attached to the backbone, into PP. By this approach it is easy to manufacture fiber-reinforced polymer composites and macro-composite components combined of metals and polymer by plastic injection moulding and compression moulding, in which good adhesion at the interface between solids and polymer is needed (Karlsson and Aström 1997, Zhou, et al. 2000). They presented the effect of the amount of PP-g-MA added into PP on the lap shear strength and on the load–displacement curves of the adhesive-bonded aluminum sheets by tensile single-lap shear test. Modification of PP by addition of 5–30 wt. % amount of PP-g-MA gives obvious promotion of the lap shear strength. It is due to the chemical interactions between –OH, Al^{3+} or amino group $–NH_2$ at the surface of the aluminum sheets and the polar functional anhydride groups and carboxylic groups –COOH on PP-g-MA at the interface. The maximum values of the lap shear strength are obtained at 20 wt. % PP-g-MA.
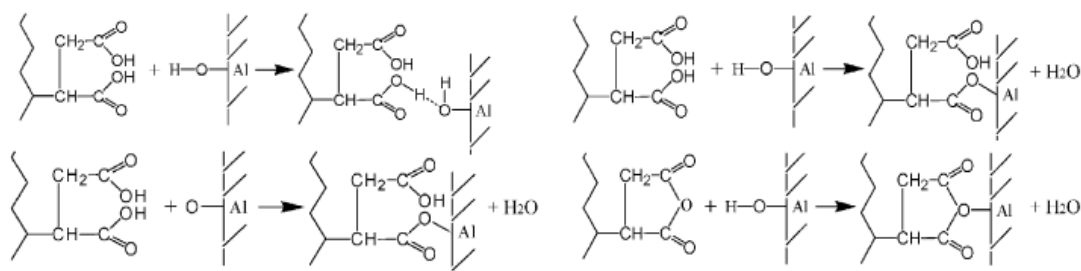
Figure 2.8. The interaction mechanism for interfacial adhesion between the functional anhydride group of PP-g-MA, the –COOH group of hydrolysed PP-g-MA and the aluminum oxide on the aluminum sheet (Source: Chen, et al. 2007)

Weager and Rudd (1999) adhered woven glass-reinforced polypropylene and aluminum by a combination of various metal surface treatments and PP-g-MA. PP-g-MA promotes brittle fracture down the metal-interlayer interface and the crack also deviates into the composite.

Reyes and Cantwell (2000) achieved adhesion between Plytron (Borealis, Norway), a unidirectional glass-fiber reinforced polypropylene, and 2024-T0 aluminum alloy by applying an amorphous chromate treatment to the aluminum and incorporating PP-g-MA at the interface. Single cantilever beam tests on model Al/GFPP laminates have shown that excellent adhesion can be achieved through the incorporation of a PP-g-MA interlayer at the bi-material interface. Based on these results, Compston et al. (2001) applied an amorphous chromate treatment to the aluminum and incorporated a layer of PP-g-MA at the E-glass fiber/polypropylene composite-aluminum interface in order to provide optimum adhesion between the layers.

Liu ve Kontopolou (2006) added PP-g-MA to improve the filler (nano silica) dispersion within the PP matrix, where the filler resided exclusively.

Rogers et al. (2005) investigated three different polypropylenes (i.e. isotactic homopolymer, maleic anhydride grafted, and silane-grafted species) with two different types of clay (a pristine and an organophilic coated) for the synthesis of partially-intercalated and exfoliated nanocomposites. The PP-g-MA exhibited the lowest contact angle, indicating low interfacial tension and good wettability. The difference in contact angle between the unmodified polypropylene and the silane-grafted polypropylene was probably due to the difference in chain mobility at the clay interface.
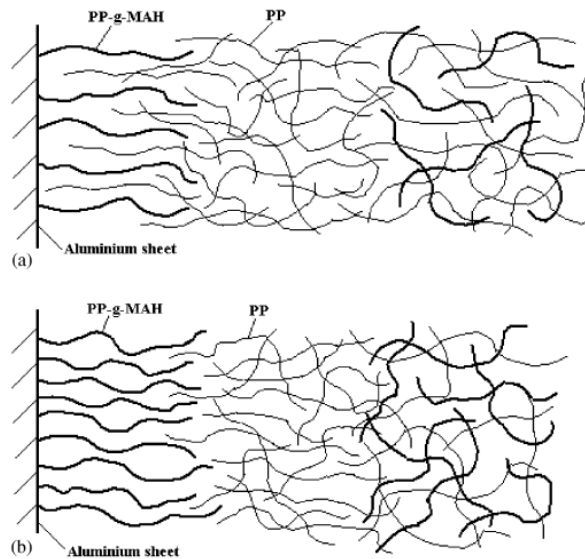
Figure 2.9.   Schematic distributions of molecules for PP with addition of PP-g-MA: a) PP with small amount of PP-g-MA b) PP with high amount of PP-g-MA (Source: Chen, et al. 2007)

Bikiaris et al. (2000) used two organofunctional silanes and a copolymer to increase the interfacial adhesion in glass fiber polypropylene (PP) reinforced composites. Coupling achieved with the copolymer PP-g-MA proved to be the most successful as compared with 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane. The combination of PP-g-MA with the silanes resulted in further property improvements because of the ability of the MA groups to react with the amino groups of the silanes.

2.2.3. Other Surface Modification Techniques

Numerous surface pretreatment techniques were developed for adhesive bonding of metals. Enhancement of the adhesion of the compound can be realized by a number of pre-treatment techniques, such as chromic acid etching, surface grafting, flame treatment, electron beam, microwave irradiation, corona discharge, glow discharge, modifying the interlayer by mechanical grinding, and by generating intermediate layers of chemically synthesized polythiophene (Chen, et al. 2007). Some of these surface treatment processes for metallic and non-metallic substrates in addition to a short description of the effect of the treatment on the material surface are shown in Table 2.4.

Table 2.4. Description of the aluminum surface pretreatments for metallic and non-metallic substrates

Substrate	Treatment Method	Effect of Treatment
Metals	Degreasing	Cleaning of the surface
Metals	Grit blast	Loose material (weak boundary) removal from the surface and increase in contact surface area
Metals	Acid etch/liquid pickling	Surface oxidation
Plastics	Corona treatment	Weak boundary layer removal and surface oxidation
Plastics	Flame treatment	Weak boundary layer removal and surface oxidation
Plastics	Chemical etching	Weak boundary layer removal and surface oxidation
Fluoroplastics	Chemical etching	Surface defluorination and oxidation

To achieve satisfactory bonding with polypropylene and similar plastics it is usually necessary to chemically modify the surfaces of these polymers, i.e., introduce chemical groups which can interact relatively strongly with the adhesives concerned. There are many methods to chemically modify the surfaces of polyolefins such as PE and PP. Several of these methods date back to about 1950; these methods include treatment with a flame, corona discharge, chromic acid immersion and exposure to chlorine gas activated by UV. The first three methods became firmly established for the treatment of PE and later PP (Adams 2005).

The corona discharge method, which involves decomposing air into active species including oxygen atoms and ozone by the application of a high voltage, is still the preferred method for treating film (Cognard 2006).

The mechanism of *flame treatment* is the thermal oxidation of the polymer surface. The flame temperature may exceed 2,000°C. It can clean the surface and remove the weak boundary layer by vaporizing surface contamination and low molecular weight polymers. Flame treatment, which involves exposing the plastic for a fraction of a second, is still widely used for treating cylindrical objects such as bottles and also for less regular shapes such as car bumpers (Ebnesajjad 2006).

In the 1960s, the use of low-pressure plasmas to improve the bondability of the polyolefins and other plastics was studied. In the 1980s interest was renewed in the uses of halogen gases to pretreat polyolefins. Treatment of PE or PP for a few seconds with mixtures of fluorine and inert gases gives large improvements in bondability. Various other pretreatments for polyolefins have been examined, although they have not found widespread industrial use. These include organic peroxides, ammonium peroxydisulphate, and sodium hypochlorite treatment (Adams 2005).

Chemical treatment or etching oxidizes the plastic surface. For instance, chromic acid is used to etch the surface of polyethylene and polypropylene. An increase in etching time and temperature intensifies the surface treatment by increasing the degree and depth of oxidation. Chromic acid has been widely used for treating three-dimensional objects, but environmental considerations make it generally unacceptable.

Reyes and Kang (2007) developed fiber metal laminates based on self-reinforced polypropylene and glass fiber-reinforced polypropylene composite materials and an aluminum alloy 2024-T3. In order to ensure a good level of adhesion, an amorphous chromate coating surface treatment was applied to the aluminum alloy prior to laminating.

Green, et al. (2002) used pre-treatment techniques for surface modification, such as corona discharge, flame, fluorination, low-pressure O/N vacuum plasma, atmospheric plasma undertaken under commercial conditions in industry and PP doped with 0.025 % and 0.05 % maleic anhydride respectively, infrared (IR) laser, silver electrolysis and proprietary coating under laboratory conditions. They examined the effects of 5 pre-treatments in detail including corono discharge, flame, gas phase fluorination, vacuum plasma and Agrodynt^{TM} (atmospheric) plasma. The PP substrates, pretreated by these 5 methods, have similar bond strengths.

Dayss et al. (1999) focused on the enhancement of the adhesion between polypropylene and copper. In their study, they carried out the modification of the polymer surface by mechanical roughening, plasma treatment or by generating intermediate layers of chemically synthesized polythiophene and plasma-polymerized acrylic acid. Mechanical roughening showed a positive effect on adhesion, but the maximum bonding strength was limited to 1 MPa. The low-pressure plasma treatment with the noble gas argon led to an enhanced adhesion. The intermediate polythiophene layer had a moderate influence on adhesion whereas the plasma-polymerized acrylic acid layer contributed excellently to adhesive forces. A combined modification of

grinding and an intermediate layer of plasma-polymerized acrylic acid led to an increased bonding strength of 3 MPa.

Weager and Rudd (1999) prepared thermoplastic composite/metal laminates by non-isothermal compression moulding of glass-polypropylene and steel or aluminum. Chromating and anodising treatments provide the strongest interfacial adhesion for aluminum, while phosphating is the better treatment for steel as shown in Figure 2.10.
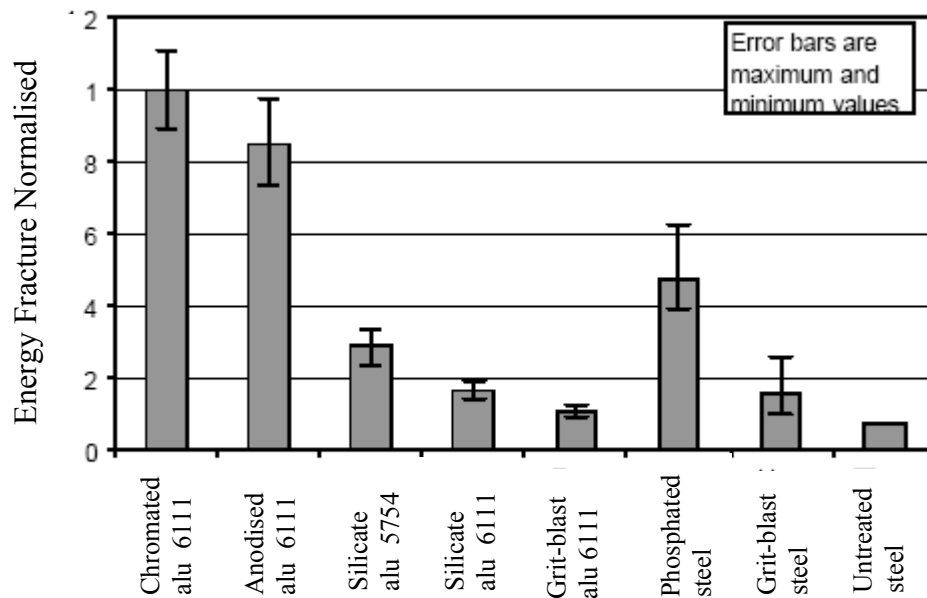
Figure 2.10. Normalised fracture energy results for glass-PP
(Source: Weager and Rudd 1999)

McKnight et al. (1993) evaluated Sulfuric-Boric Acid Anodizing (SBAA) and Phosporic Acid Anodizing (PAA) as alternative surface treatments besides the use of silane coupling agents. SBAA was shown to be an effective non-chromate based surface treatment for bonding aluminum with PP. Durability of joints using SBAA treated aluminum was better than exhibited by PAA-treated adherends.

2.3. Test Techniques for Evaluating Effectiveness of Adhesive Joining Methods

The physical testing of standard adhesive joints provides a method of comparison for materials and processes that are being evaluated. Standard tests also

provide a means to control the adequacy of the bonding process, once it is established, and of assessing its conformance to specification (Petrie 2000).

For structural joints, strength is typically evaluated using shear tests (for static properties and fatigue) and toughness with cleavage tests (Baker, et al. 2002).

2.3.1. Lap-shear tests

The lap-shear or tensile-shear test measures the strength of the adhesive in shear. It is the most common adhesive test because the specimens are inexpensive, easy to fabricate, and simple to test (Rosselli 2006).

The lap shear specimen can be used for determining shear strength of dissimilar materials. Thin or relatively weak materials such as plastics, rubber, or fabrics are sandwiched between stronger adherends and tested.

There are two main specifications, one for metals, ASTM D 1002 (Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading) and the other for plastics, ASTM D 3163 (Standard Test Method for Determining Strength of Adhesively Bonded Rigid Plastic Lap-Shear Joints in Shear by Tension Loading). ASTM D 3164 (Strength Properties of Adhesively Bonded Plastic Lap-Shear Sandwich Joints in Shear by Tension Loading) extend the application of test method ASTM 3163 to single-lap-shear adhesive joints employing plastic adherends (Rosselli 2006).

In these standarts, testing is carried out by pulling the two ends of the overlap in tension causing the adhesive to be stressed in shear. Tension is applied along the length of the coupon as shown in Figure 2.11. Hence, these tests are frequently called the tensile-shear test. Since the test calls for a sample population of five, specimens can be made and cut from larger test panels.
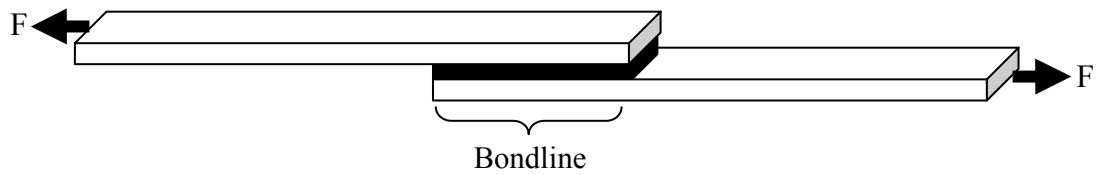
Figure 2.11. Schematic of a lap-shear ASTM D 1002/3163/3164 coupon under tensile loading

2.3.2. Peel tests

Peel testing can be helpful for examining the brittleness of an adhesive and energy release rate (peel resistance). Peel resistance is important for many commercial applications and there are many types of tests based on the substrate stiffness. In any case, a bonded joint must be designed to reduce or eliminate peel loads. However, peel cannot be avoided in many practical cases and a fastener should be placed at the edge of the bonded assembly to reduce peel loading on the adhesive (Rosselli 2006).

The most common method used to assess the relative performance of an adherend surface pretreatment involves loading an adhesive joint asymmetrically in tension, as shown in Figure 2.12, described as mode I opening. Peel tests involve stripping away a flexible adherend from another adherend that may be flexible or rigid. The specimen is usually peeled at an angle of 90 or 180 degrees (Petrie 2000).
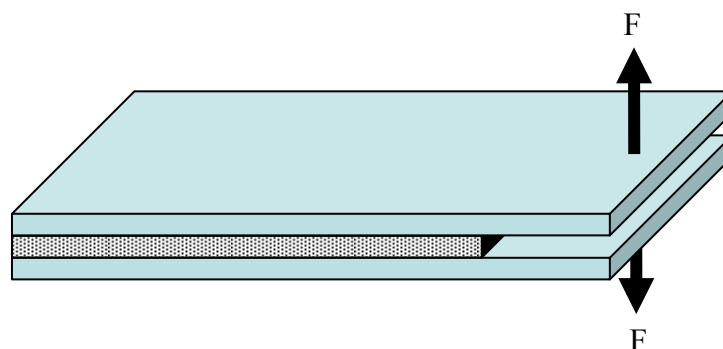
Figure 2.12. Asymmetric tension or mode I opening of an adhesive joint

ASTM D 3807 (Standard Test Method for Strength Properties of Adhesives in Cleavage Peel by Tension Loading) covers the determination of the comparative cleavage/peel strengths of adhesives bonded to engineering and reinforced plastics (Rosselli 2006).

Laminated test panels consist of two semi-rigid adherands bonded as shown in Figure 2.13. Load is applied so that the crack initiation load and average crack propagation load (cleavage/peel resistance) over at least a 51 mm (2 inch) length of bond line are recorded (Rosselli 2006).

The mechanical performance of a bond should be accompanied by an inspection of the fracture surface. Visual inspection assisted with optical microscopy will provide macroscopic information concerning the locus of fracture and the presence of voids or defects (Baker, et al. 2002).
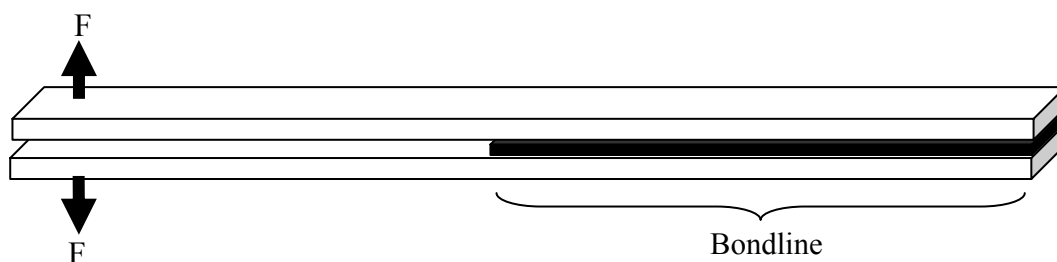
Figure 2.13. Schematic of ASTM D 3807 cleavage peel test sample subjected to loading

CHAPTER 3

EXPERIMENTAL

3.1. Materials

The laminates were manufactured from sheets of 2 and 4 mm thick aluminums (Al) and a woven cloth consisting of co-mingled glass and polypropylene fibers (GFPP) with a fiber volume fraction of 60 wt. %. Biaxial stitched +45°/-45° non-woven glass-polypropylene fabrics as schematically illustrated in Figure 3.1 was prepared in coloboration with Telateks Inc. of Turkey. Properties of glass-polypropylene non-crimp hybrid fabrics are given in Table 3.1. The glass fibers were used as reinforcement constituent to fabricate polypropylene matrix composite panels.
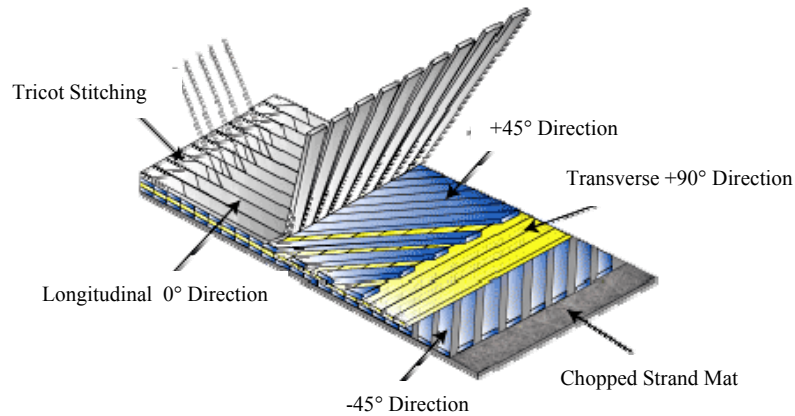
Figure 3.1. Schematic illustration of biaxial stitched non-crimp glass-PP fabrics
(Source: Vectorply 2009)

A closed-cell aluminum foam material (supplied by Shinko Wire Company Ltd., Japan) with the trade name Alulight was used in this study. A silane coupling agent, N-(4-vinylbenzyl)-N9-(3-trimethoxysilylpropyl)-ethylenediamine hydrochloride (Z-6032) as illustrated in Figure 3.2, was provided from Dow Corning™. Distilled water and glacial acetic acid was used in order to prepare silanol solution.

Table 3.1. Properties of co-mingled glass-PP fabrics used in this study

Fibers	Tex (g/10000m)	Composition by Weight (%)	Nominal Weight (g/m^2)	Weaving Angle
Glass	300	60	767	+45°/-45°
PP	200	40		

$$(CH_3O)_3 - SiCH_2\ CH_2\ CH_2\ NCH_2\ CH_2N - R_2$$
$$|$$
$$R$$

where R is either hydrogen or

—⟨O⟩— CH = CH$_2$ - HCl
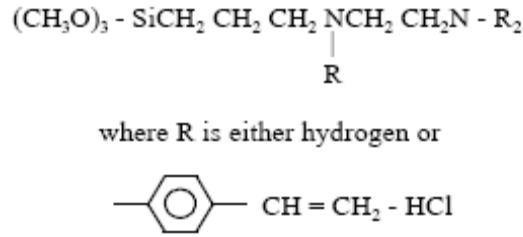
Figure 3.2. Chemical structure of Dow Corning™ Z6032 silane

(Source: Dow Corning 2009)

A polyolefin based adhesive film (Bemis 6218) was supplied from Bemis Associates Inc., USA. Dupont^{TM} Fusabond$^®$ P613, a maleic anhydride modified polypropylene (PP-g-MA) was obtained in granular form . The general properties of the Fusabond$^®$ P613 are a density of 0.902 g/cm^3, and a melting point (T_m) of 162°C. The polypropylene (MH418) which is an injection grade of homopolymer with a density 0.855 g/cm^3 and melting point of 160°C was provided by PETKİM Petrochemicals, Turkey.

3.2. Preparation Technique of Layered Structures

3.2.1. Surface Treatment of Aluminum

Aluminum (Al) surfaces were treated with silane coupling agent in order to improve the adhesion between the polymer matrix and Al. Al surfaces were firstly degreased, and then modified with silane treatment. The surface modification procedure

is schematically illustrated in Figure 3.3. Silane treatment was applied based on product information of Dow Corning Z-6032 silane (Dow Corning).
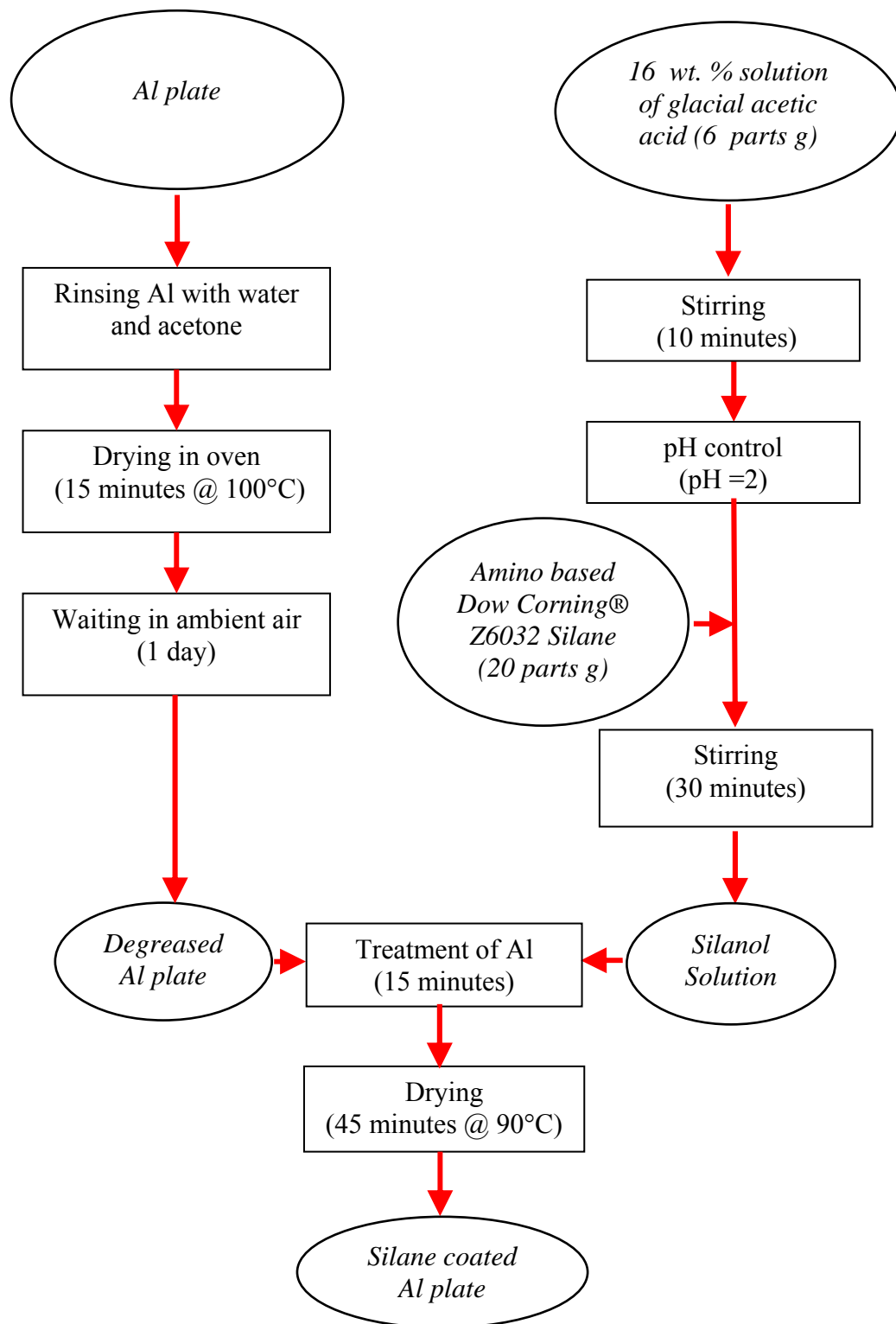
Figure 3.3. Schematic of silane surface treatment procedure

The Al surfaces were treated with acetone at room temperature for fully degreasing and rinsed with water to provide a neutral bonding surface. The Al samples were dried and held in an air-circulating oven at 100°C for 15 minutes. After waiting for 1 day in ambient air, they were ready to be coated with silane.

In order to prepare Z-6032 silane solution, 16 wt. % solution of glacial acetic acid was prepared with a ratio of 1 parts glacial acetic acid to 5 parts distilled water under continuous stirring for 10 minutes. pH of the solution was set to 2 by incorporation of 20 parts Z-6032 silane coupling agent into to the 16 wt. % solution of glacial acetic acid. They were blended using mechanical stirrer for another 30 minutes.

The degreased Al plates were dipped into the prepared Z-6032 silane solution and they were left with in the solution for 15 minutes. After removal of the samples from the solution, the samples were then dried at 90°C for 45 minutes, which is an effective drying cycle for this silane coupling agent.

Figure 3.4. Photo of the extruder (Axon AB Plastic Machinery) used to obtain PP/PP-g-MA films

In order to incorporate maleic anhydride modified polypropylene (PP-g-MA) layer at the Al-GFPP interface, firstly 20 wt. % PP-g-MA films were prepared. Neat PP was blended with PP-g-MA in an Axon AB single screw extruder (Plastic Machinery, Sweden) as illustrated in Figure 3.4. The extruder has an L/D of 20, and a diameter of 18 mm. The experimental conditions of the extrusion process are given in Table 6.3. PP and PP-g-MA were mixed by weight ratio of 20 % of PP-g-MA. The 20 wt. % PP-g-MA blend was collected at the exit of the extruder and left for cooling at room temperature. The cooled blend was pressed at the 175°C under the fixed pressure of 1 MPa by Carver press (Figure 3.5) to obtain 200x200mm samples. The prepared film had

an average thickness of 0.5 mm. It is important to place Kapton^{TM} film on the mold surface to remove the film easily from the pres shown in Figure 3.6.

Table 3.2. Experimental conditions of the extrusion process

Screw Frequency (Hz)	Motor Voltage (V)	Motor Current (A)	Roller Frequency (Hz)	Zone Temperatures (°C)					
				1	2	3	4	5	6
20	38	4.5	4-7	200	200	200	200	200	200

Figure 3.5. Photo of the hot pres (Carver^{TM}) used to prepare films

Figure 3.6. Photo of production stages of PP based film containing 20 wt. % PP-g-MA a) blend obtained after extrusion b) blend between Kapton^{TM} films before pressing c) PP based film containing 20 wt. % PP-g-MA obtained

Polyolefin based adhesive film was placed between the composite and degreased Al plate as illustrated in Figure 3.7.

```
          ┌─────────────────────┐
          │      Al plate       │
          └─────────────────────┘
                     │
                     ▼
         ┌──────────────────────┐
         │  Rinsing Al with water│
         │     and acetone       │
         └──────────────────────┘
                     │
                     ▼
         ┌──────────────────────┐
         │    Drying in oven     │
         │ (15 minutes @ 100°C)  │
         └──────────────────────┘
                     │
                     ▼
         ┌──────────────────────┐
         │  Waiting in ambient air│
         │       (1 day)         │
         └──────────────────────┘
                     │
                     ▼
          ┌─────────────────────┐
          │     Degreased Al    │
          │        plate        │
          └─────────────────────┘
                     │              ┌─────────────────────┐
                     │◄─────────────│  Polyolefin based   │
                     │              │   adhesive  film    │
                     │              │    (Bemis 6218)     │
                     │              └─────────────────────┘
                     ▼
         ┌──────────────────────┐
         │  Placement of polyolefin│
         │  based adhesive  film │
         │     (Bemis 6218)      │
         │   into the interlayer │
         └──────────────────────┘
                     │
                     ▼
         ┌──────────────────────┐
         │  Hot pressing @ 145°C │
         │      for 5 hour       │
         └──────────────────────┘
                     │
                     ▼
      ┌────────────────────────────┐
      │ Polyolefin based adhesive film│
      │   (Bemis 6218) incorporated   │
      │   composite/metal laminates   │
      └────────────────────────────┘
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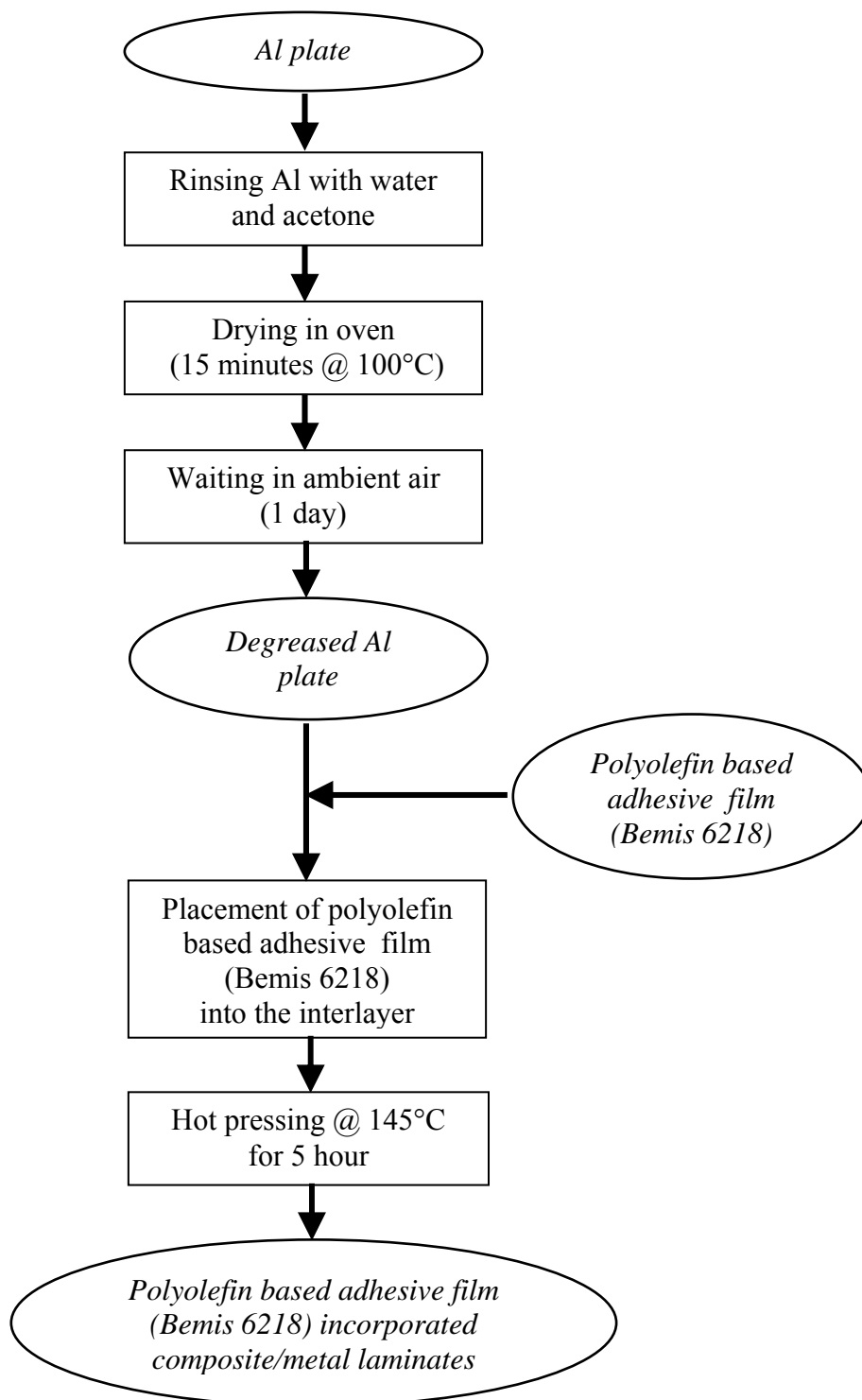
Figure 3.7. Schematic of incorporation of polyolefin based adhesive film (Bemis 6218) at the composite/metal interface
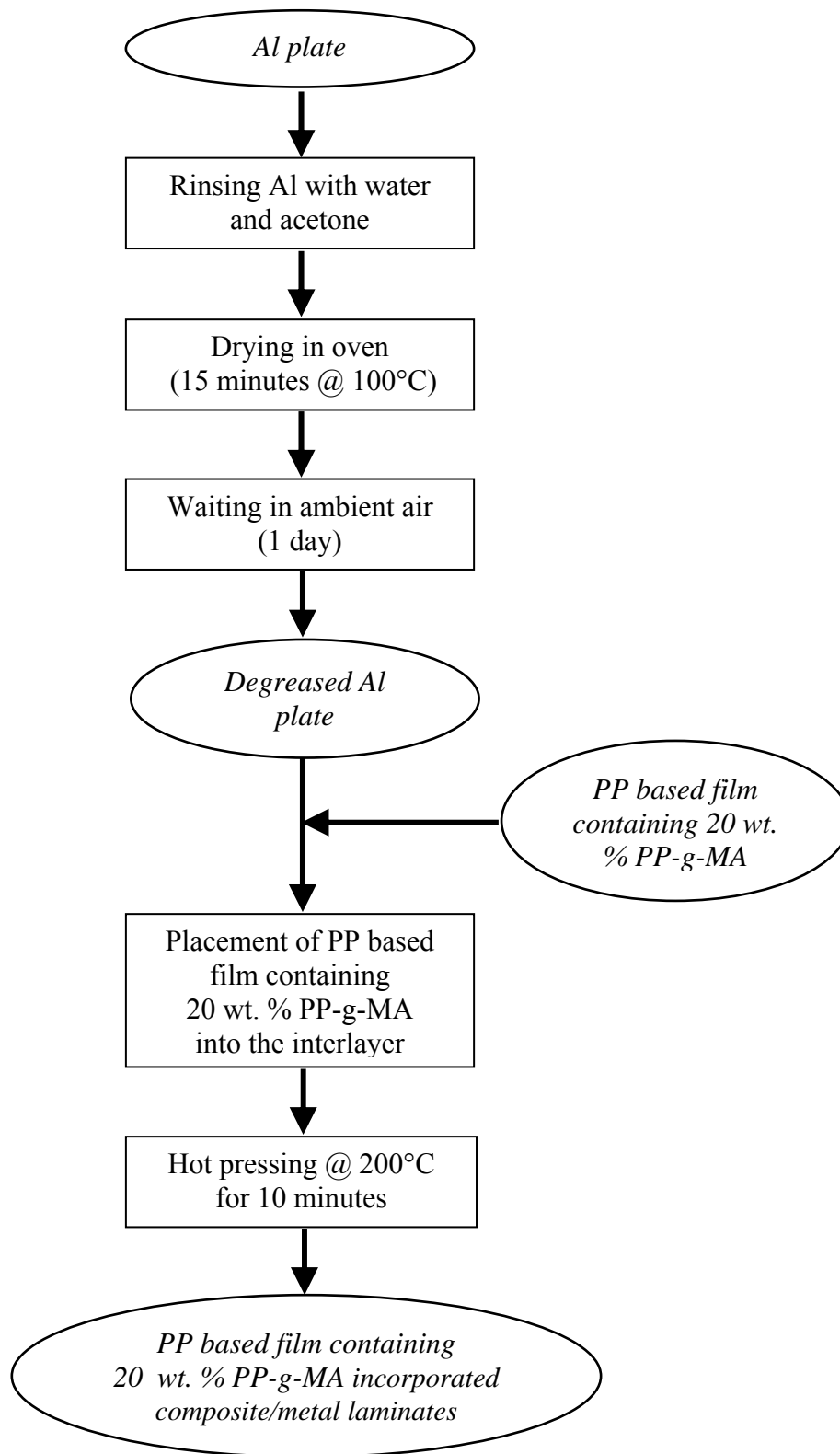
Figure 3.8. Schematic of incorporation PP based film containing 20 wt. % PP-g-MA layer at the GFPP composite/metal interface

The schematic of incorporation of 20 wt. % PP-g-MA film at the composite/metal interface is illustrated in Figure 3.8. At first Al surfaces were cleaned with acetone and rinsed with water as described before. After drying in oven at 100°C for 15 minutes, the plates were left in ambient air for 1 day. PP based film containing 20 wt. % PP-g-MA were placed onto the degreased Al and pressed together with GFPP composites.

3.2.2. Fabrication of Layered Structures

The laminated composites were manufactured from sheets of 2 or 4 mm thick Al plate and a woven cloth consisting of co-mingled glass and polypropylene fibers (GFPP) as illustrated in Figure 3. 9.
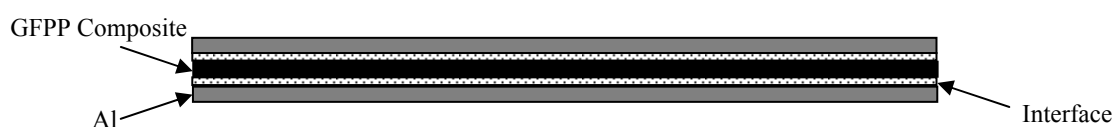
Figure 3.9. Schematic illustration of Al/GFPP laminated composites

The various layers of Al and GFPP were stacked together, and hot pressed to the processing temperature of the composite (200°C) for 10 minutes at a constant pressure of 1.5 MPa by Carver Press. So, melting of PP fibers and formation of GFPP composite occured during the lamination process of the sandwich structure. After lamination, the parts were cooled down to room temperature at a constant cooling rate of 15°C/min under the fixed pressure of 1.5 MPa.

On the other hand in the case of laminates containing polyolefin based adhesive film, GFPP composite was prepared with in an initial stage before lamination of the sandwich structure due to processing temperature of the polyolefin based adhesive film (145°C). During final lamination process, Al-polyolefin based adhesive film and GFPP were hot pressed at 145°C for 5 hours at a constant pressure of 1.5 MPa. After lamination, similarly, the parts were cooled down to room temperature at a constant cooling rate of 15°C/min under the fixed pressure of 1.5 MPa.

3.3. Mechanical Property Characterization

3.3.1. Lap Shear Strength Testing

The lap shear test was performed to evaluate the interfacial properties of laminates with various surface treatments. The specimen geometries of the tensile single lap shear tests were selected in accordance to ASTM D 3164-03 Standard. Lap-shear test panels were prepared from 2 mm thick Al plate and 2 plies of GFPP. Silane treated Al plates were prepared based on the procedure described before. GFPP and Al plates with and without silane treatment were conformed to the form and dimensions as depicted in Figures 3.10 and 3.11.
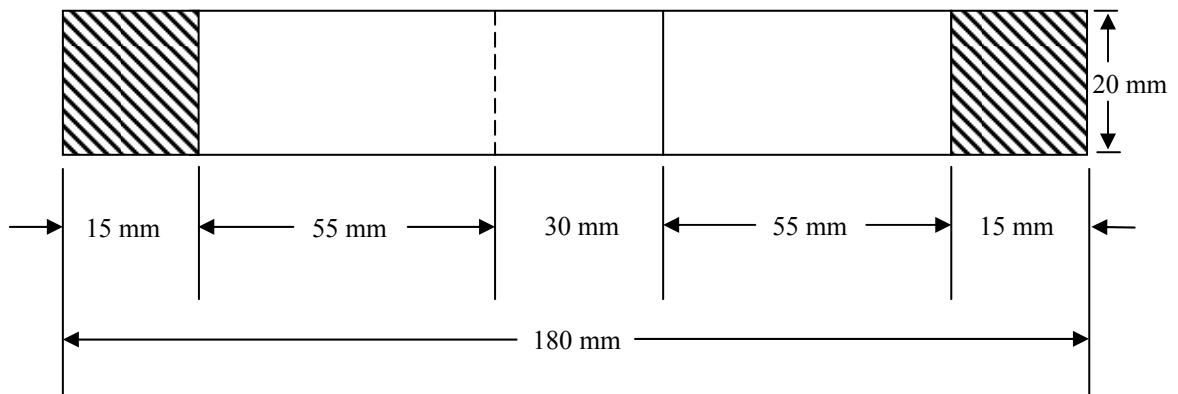
Figure 3.10. Schematic of lap-shear test specimen
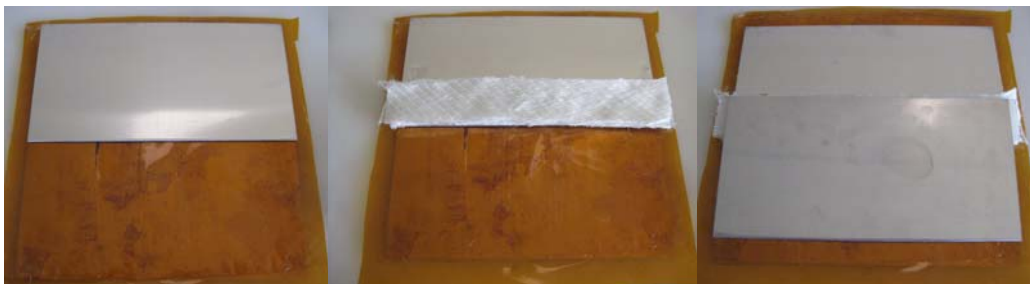
Figure 3.11. Photo of lap-shear test panel preparation

After hot-pressing of the laminates, lap-shear specimens (20 mm in width) were cut from the test panel by a metal saw (Figure 3.12). Laminates with PP-g-MA film was also obtained based on the procedure described before.

The shear force–displacement data were collected and stored as data files. Shear strength was calculated based on the maximum load divided by the area of bonded overlap. At least five specimens were tested and average value and the standard deviations were calculated.

Figure 3.12. Photo of lap-shear test specimens

The shear strength testing was performed using the Schimadzu AGI universal test machine (5 kN) as shown in Figure 3.13. The test was performed with a crosshead speed of 1.3 mm/min.

Figure 3.13. Lap shear strength test specimen loaded with Schimadzu AGI universal test machine (5 kN)

3.3.2. Peel Test

Peel testing was performed to determine the strength of adhesives in cleavage peel by tension loading. In order to characterize the adhesion between the Al and the GFPP composite, the specimens were prepared according to ASTM D3807 Standard. Figure 3.14 schematically illustrates the peel test specimen configuration. Before laminating, Al plates were cut 26 mm in width and 180 mm in height as shown in Figure 3.15. Laminated test panels consist of two 4 mm thick aluminums and two plies GFPP were bonded in accordance with the procedures described before. A crack approximately 77 mm in length was induced by the placement of a Kapton[TM] film between GFPP and Al before bonding.
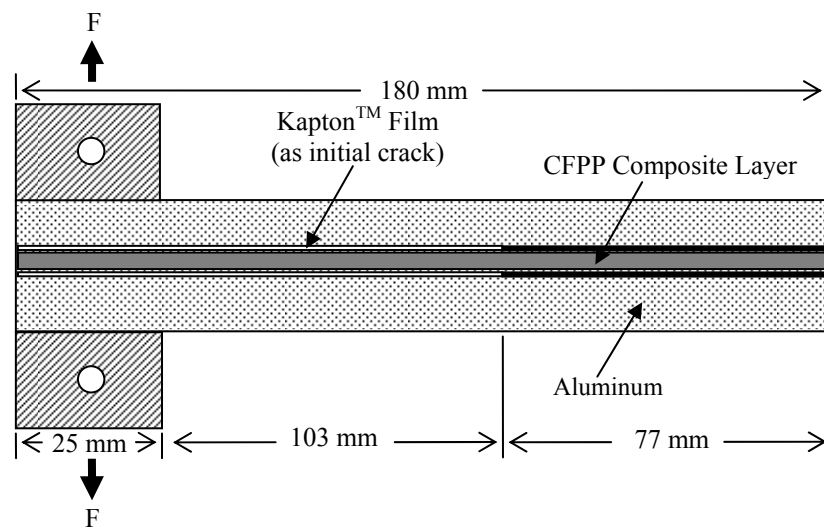
Figure 3.14. Schematic of the peel test specimen
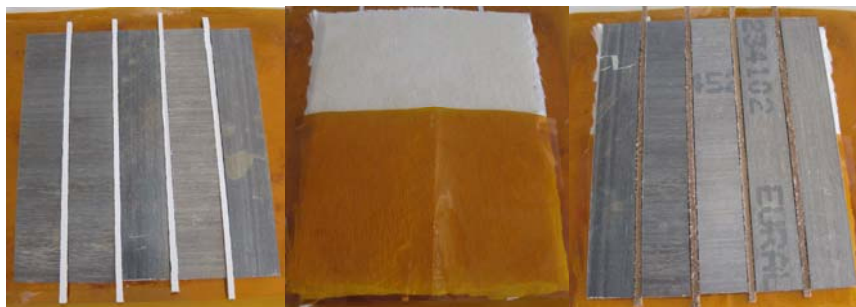
Figure 3.15. Images from the peel test specimen preparation

The peel test specimens were sectioned from Al/GFPP composite laminates with 26 mm in width and 180 mm in length. At least five specimens of Al/GFPP composite laminates including silane treated and modified with PP-g-MA and incorporated polyolefin based adhesive film were tested using the Schimadzu AGI universal test machine with a crosshead speed of 12.7 mm/min as shown in Figure 3.16. The load-displacement datas were recorded and average peel strength values were calculated.
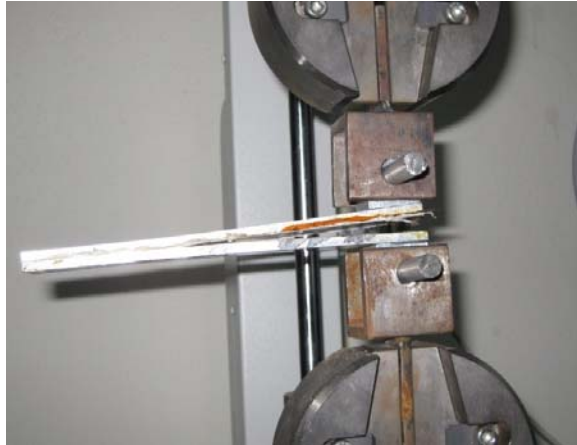
Figure 3.16. Peel test specimen loaded under load

3.3.3. Bending Test

The three-point bending tests based on ASTM D 790M Standard were carried out using Schimadzu AGI universal test machine. The load-displacement curves were obtained for all samples. For this purpose, GFPP was hot pressed between 2 mm thick Al plates that exposed to different surface pretreatment techniques as described before. Test panels approximately were sectioned in 10 width and 100 mm length (Figure 3.17).

Figure 3.17. Images of the bending test specimen preparation

The bending test specimens were loaded with a crosshead speed of 2.1 mm/min (Figure 3.18). Support span (L) was determined as 80 mm. The bending strength (S) were calculated by the following equation,

$$S = 3FL/2bd^2 \qquad (3.1)$$

where F is the maximum load on the load-displacement curve (N), b is the width of beam tested (mm), d is the depth of beam tested (mm) as shown in Figure 3.19. Load-displacement graphs were obtained during the test.
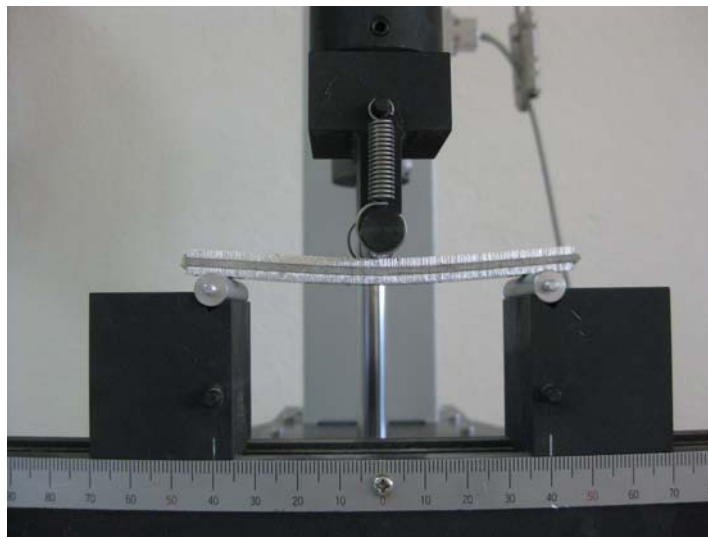
Figure 3.18. Bending test specimen under load
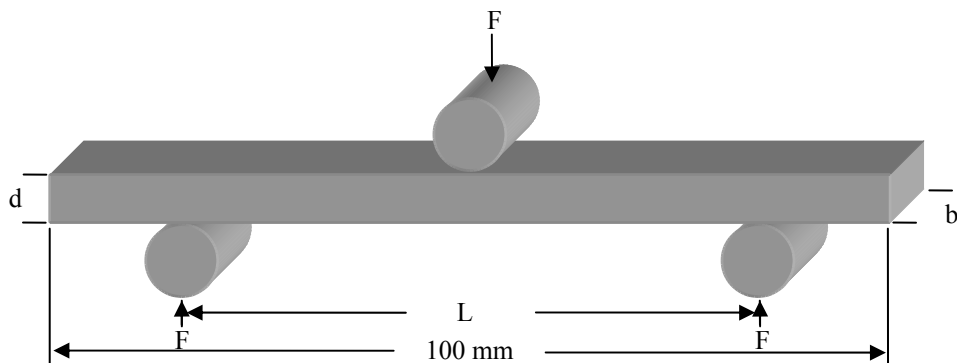
Figure 3.19. Schematic of the bending test specimen

3.4. Microstructure Characterization

Digilab Excalibur series (FTS-3000) Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) was used to investigate untreated and silane treated Al surfaces.

Cross sections of the laminated structures with different surface pretreatments were examined by Nikon^{TM} optical microscope. Initially the cross sections of the specimens were polished to obtain clear images.

Phillips™ Scanning Electron Microscope (SEM) was used to examine the fracture surfaces of tested specimens. All of the specimens were coated with a very thin layer of gold by sputtering technique prior to SEM investigations to obtain a conductive surface.

CHAPTER 4

RESULTS AND DISCUSSION

Polypropylene (PP) is an inactive material to bond surfaces such as metals and ceramics due to the lack of reactive groups on the polymer chains. So primary bonding does not occur between aluminum (Al) and glass fiber reinforced polypropylene composites (GFPP). In this chapter, the effects of various surface modification techniques to improve adhesive properties between Al and GFPP are presented.

4.1. Mechanical Properties of Al/GFPP Interfaces

4.1.1. Interfacial Lap Shear Strength

Interfacial shear stress vs. displacement values of silane treated Al adherends bonded with GFPP is illustrated in Figure 4.1. As seen in Figure 4.1, with increasing displacements, shear stress values of silane treated Al/GFPP increased in a stable manner until failure point. Sudden drops were observed at about 1.5 mm displacement. Shear strength values were obtained from the maximum shear stresses of each of the samples and are tabulated in Table 4.1, together with average values. Untreated Al/GFPP samples exhibited almost no bonding between Al and GFPP as given in Table 4.1. As seen from Table 4.1, interfacial shear strength value of 2.03 N/mm^2 is obtained by silane treatment of Al surfaces. It is concluded that amino based silane (Z-6032) provided significant improvement in interfacial shear stresses over the untreated specimens. This improvement was due to the chemical bonding between polypropylene and the amino group of the Z-6032 silane as expected. Aminofunctional silane coupling agents form a polysiloxane layer probably on the Al surface due to the catalytic effect of the amino group in the polycondensation process (Demjen, et al. 1999).
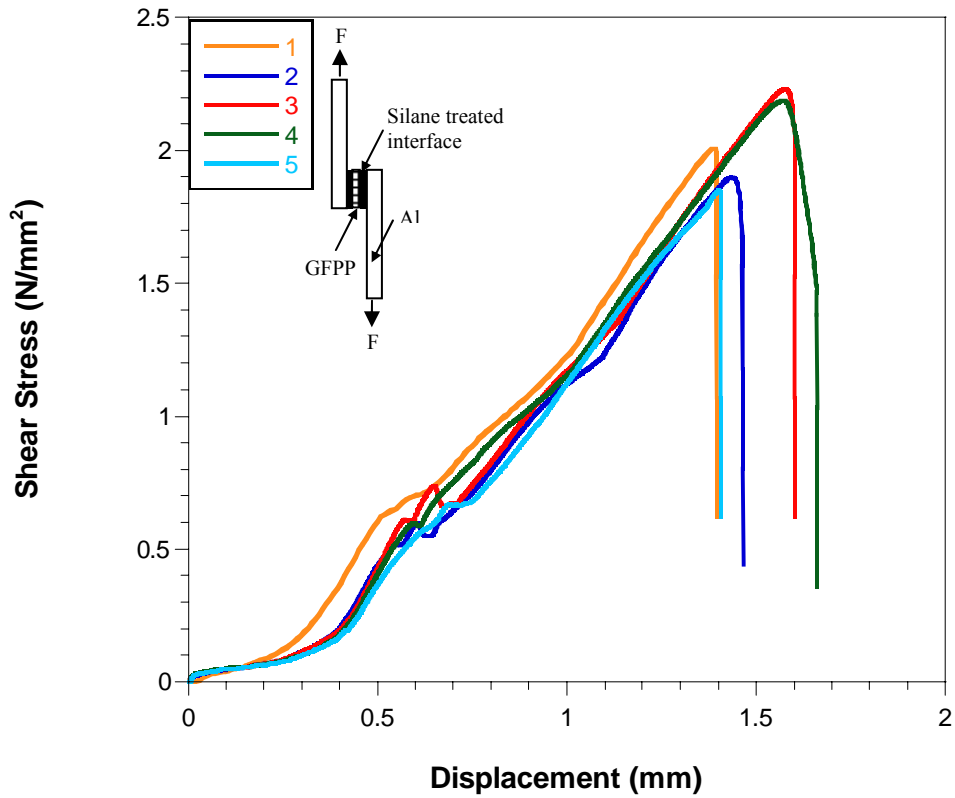
Figure 4.1. Interfacial shear stress vs displacement values for silane treated Al/GFPP
interfaces (numbers indicate that five samples tested from the same batch)

As an alternative method, polyolefin based adhesive film was incorporated as an interlayer between Al and GFPP. The interfacial shear stress vs. displacement values are shown in Figure 4.2. The interfacial shear stress values of Al/GFPP interfaces with polyolefin based adhesive film remains constant at about 0.1 N/mm^2 up to 0.3 mm displacement and then start to increase in a stable manner up to maximum 0.62 N/mm^2 where sudden drops occurs. As compared to the others, polyolefin based adhesive film gave the lowest interfacial shear strength value (0.57 N/mm^2) as illustrated in Table 4.1. Also, the displacements at the maximum shear stress values were found to be the lowest as compared to those with other pretreatment techniques. This may be related with low process temperature of polyolefin based adhesive film (145°C) which is under the melting point of PP (165°C). So no melting on the surface of GFPP during lamination may cause to the poor adhesion. Besides, it is not possible to increase the process temperature of polyolefin based adhesive film (145°C) above the melting temperature of the GFPP (200°C) because polyolefin based adhesive film has a melting point of 66°C and degredation at elevated temperatures occurs.
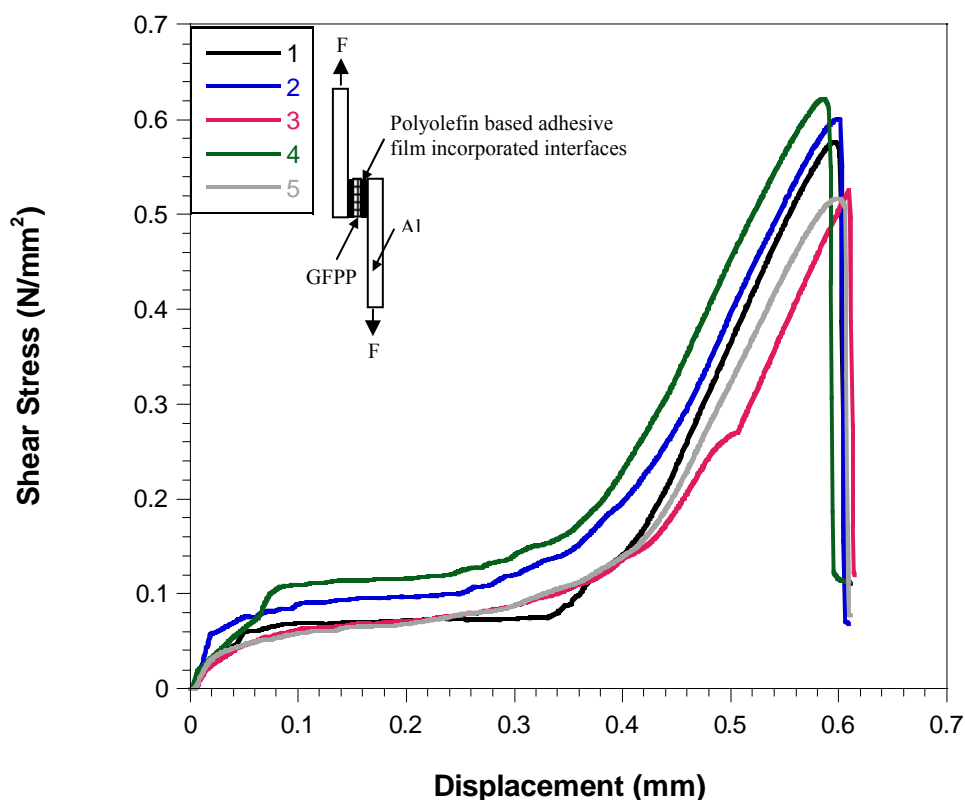
Figure 4.2. Interfacial shear stress vs displacement values for polyolefin based adhesive film incorporated Al/GFPP interfaces (numbers indicate that five samples tested from the same batch)

Figure 4.3 shows the effect of PP-g-MA based layer modification on the lap-shear strength of the adhesive-bonded Al/GFPP. From the figure, it is seen that shear stress values of Al/GFPP interface modified with PP based film containing 20 wt. % PP-g-MA rises continuously until break points. Interfacial shear strength value is reached to 5.93 N/mm^2 as listed in Table 4.1. For this type of samples displacement values at which maximum stress (2.9 mm) also increased as compared with other pretreatment techniques. Based on this results, it can be concluded that the introduction of PP based film containing 20 wt. % PP-g-MA into the Al/GFPP interlayer results in substantial improvement of the fracture strength and toughness of the adhesive joint. The increase of the lap shear strength can be ascribed to the contribution of chemical interactions at the interface. Also, due to good adhesion at the interface plastic deformation of the interlayer material or matrix occurs that leads to high toughness values.
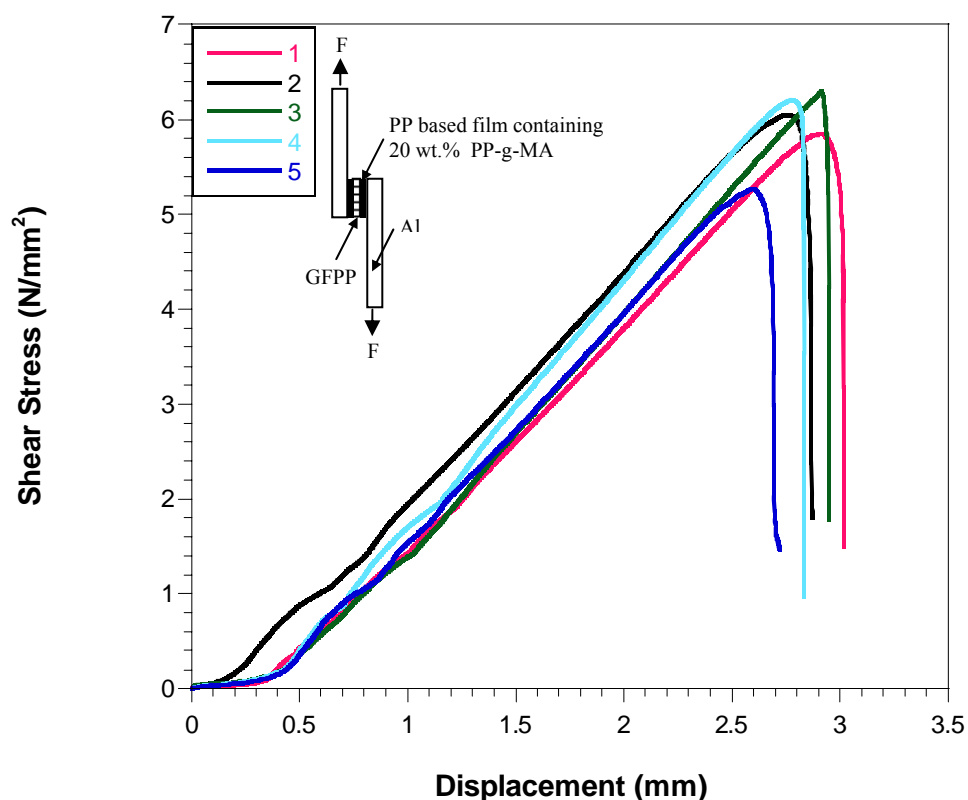
Figure 4.3. Interfacial shear stress vs displacement values for Al/GFPP laminates modified with PP-g-MA (numbers indicate that five samples tested from the same batch)

Table 4.1. Shear strength values for Al/GFPP interfaces silane treated, polyolefin based adhesive film incorporated and modified with PP-g-MA

Sample Al/GFPP	Shear Strength (N/mm^2)			
	Untreated	Silane treated	Polyolefin based adhesive film incorporated	Modified with PP-g-MA
1	No bonding	2.01	0.58	5.85
2	No bonding	1.89	0.60	6.04
3	No bonding	2.23	0.53	6.30
4	No bonding	2.19	0.62	6.20
5	No bonding	1.85	0.52	5.27
Average	-	**2.03**	**0.57**	**5.93**
Standard Deviation (+/-)	-	0.17	0.05	0.41

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4.1.2. Peel Strength of Al/GFPP and Al-foam/GFPP Laminates

Typical load-displacement graphs obtained during peel test are illustrated in Figures 4.4 to 4.6 for Al/GFPP laminates with silane treated, polyolefin based adhesive film incorporated and modified with PP based film containing 20 wt. % PP-g-MA, respectively. Peel-strength values for each of the samples were calculated and tabulated in Table 4.2 together with average values. Peel strength values were found as zero for untreated Al/GFPP samples as given in Table 4.2 indicating no bonding between Al and GFPP. The peel strength values of Al/GFPP silane treated, polyolefin based adhesive film incorporated and modified with PP based film containing 20 wt. % PP-g-MA were increased to 0.53, 2.67, and 6.61 N/mm, respectively. The load-displacement graph of silane treated Al/GFPP laminates exhibits saw-tooth appereance associated with unstable crack propogation.
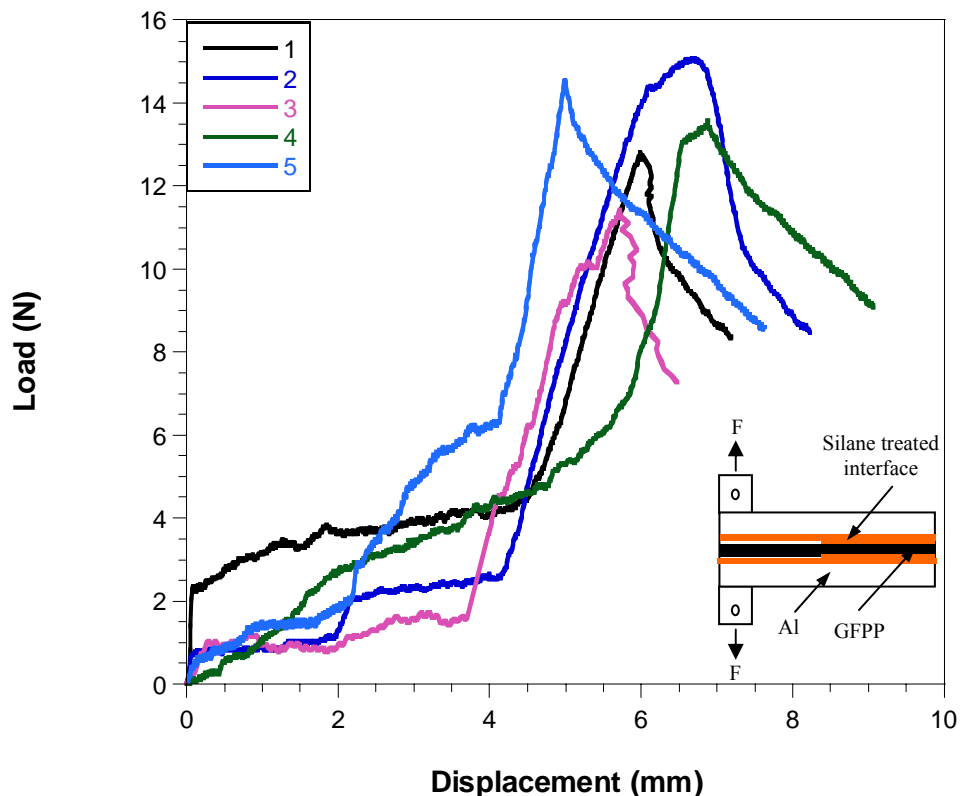
Figure 4.4. Load – displacement graphs obtained during peel testing for silane treated Al/GFPP (numbers indicate that five samples tested from the same batch)
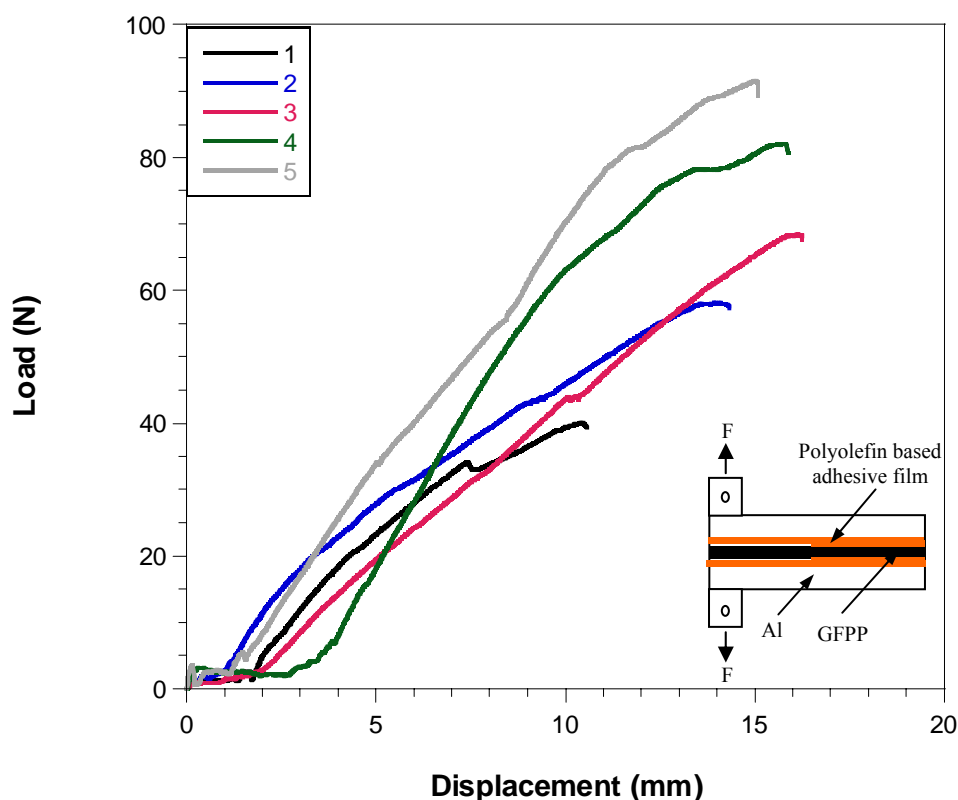
Figure 4.5. Load – displacement graphs obtained after peel testing for polyolefin based adhesive film incorporated Al/GFPP (numbers indicate that five samples tested from the same batch)

Load vs. displacement graphs for Al/GFPP laminates modified with PP based film containing 20 wt. % PP-g-MA exhibited a much smoother increase of the load as compared to those treated with other techmiques. Also these samples exhibited the highest displacement and stress values at break. As seen from Table 4.2, Al/GFPP exhibits highest peel strength value (6.61 N/mm) with PP-g-MA modification. Weager and Rudd (1999) determined maximum loads as higher than 120 N with PP-g-MA interlayer. Reyes and Cantwell (2000) determined fracture energy values approaching 2200 J/m^2 and concluded that good adhesion is achieved between Al/GFPP interface by the incorporation of PP-g-MA layer.

Figure 4.6. Load – displacement graphs obtained after peel testing for Al/GFPP modified with PP-g-MA (numbers indicate that five samples tested from the same batch)

Table 4.2. Peel strength values for Al/GFPP interfaces silane treated, polyolefin based adhesive film incorporated and modified with PP-g-MA

Sample Al/GFPP	Peel Strength (N/mm)			
	Untreated	Silane treated	Polyolefin based adhesive film incorporated	Modified with PP-g-MA
1	No bonding	0.50	1.57	6.70
2	No bonding	0.59	2.28	7.13
3	No bonding	0.45	2.68	5.79
4	No bonding	0.53	3.22	7.10
5	No bonding	0.57	3.59	6.35
Average	**-**	**0.53**	**2.67**	**6.61**
Standard Deviation (+/-)	**-**	0.06	0.79	0.56

Figures 4.7 to 4.9 show the peel test load-displacement curves for Al-foam/GFPP laminates with silane treated, polyolefin based adhesive film incorporated and modified with PP-g-MA, respectively. Although, a stable crack propogation was observed with other samples, bending of Al foam layers occurred for Al foam/GFPP samples modified with PP-g-MA as seen in Figure 4.10. Peel strength values of the laminates containing Al-foam are presented in Table 4.3. The peel strength of silane treated Al-foam/GFPP laminate (1.01 N/mm) exhibited two times greater values than those with silane treated Al/GFPP laminate (0.53 N/mm). This may be related with the surface roughness of the Al foams. However, a reduction in peel strength of polyolefin based adhesive film incorporated Al-foam/GFPP laminate (0.91 N/mm) was measured as compared to those with Al layer (2.67 N/mm). For the laminates with PP-g-MA, the peel strength was found to be over 1.75 N/mm. So, due to the best adhesion between Al-foam and GFPP surfaces with PP-g-MA interlayer, peeling at the interface does not occur, but bending of the Al-foam is observed at critical bending stresses.

Figure 4.7. Load – displacement graphs obtained after peel testing for silane treated Al-foam/GFPP (numbers indicate that five samples tested from the same batch)
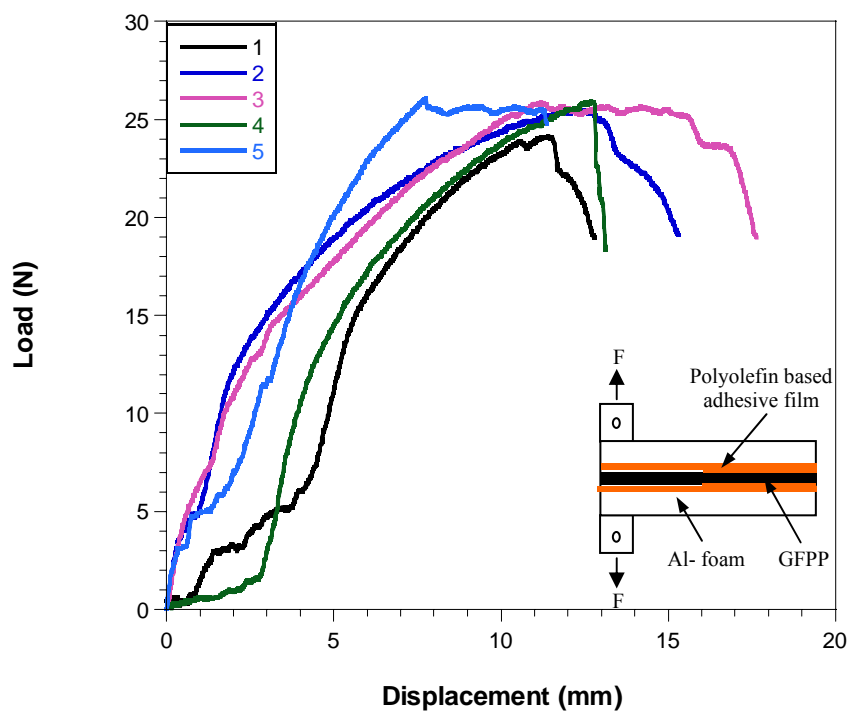
Figure 4.8. Load – displacement graphs obtained after peel testing for polyolefin based adhesive film incorporated Al Foam/GFPP (numbers indicate that five samples tested from the same batch)
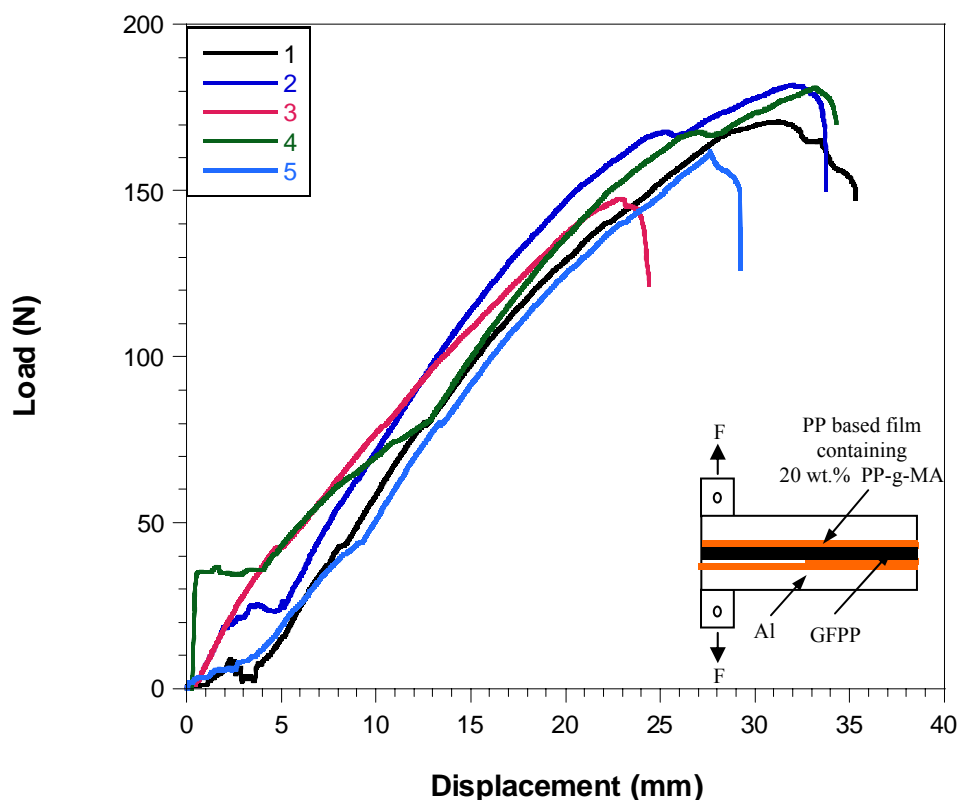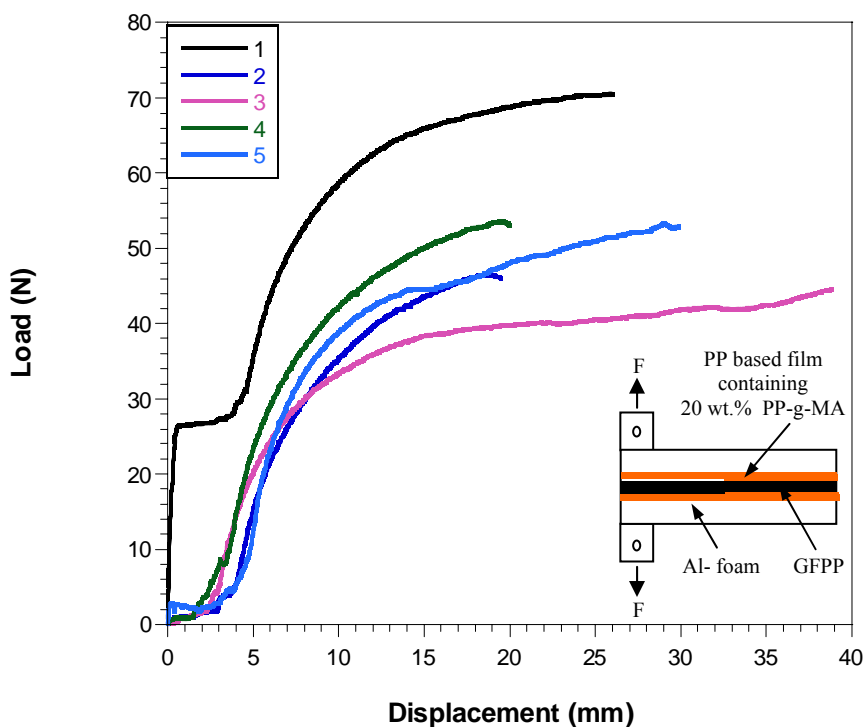

Figure 4.9. Load – displacement graphs obtained after peel testing for Al-foam/GFPP modified with PP-g-MA (numbers indicate that five samples tested from the same batch)

Table 4.3. Peel strength values for Al Foam/GFPP laminates with silane treated, polyolefin based adhesive film incorporated and modified with PP-g-MA

Sample Al-foam /GFPP	Peel Strength (N/mm)			
	Untreated	Silane treated	Polyolefin based adhesive film incorporated	Modified with PP-g-MA
1	No bonding	0.82	0.95	over 2.77
2	No bonding	0.76	0.60	over 1.83
3	No bonding	1.01	1.00	over 1.75
4	No bonding	0.98	1.01	over 2.10
5	No bonding	1.51	1.02	over 2.09
Average	-	**1.01**	**0.92**	-
Standard Deviation (+/-)	-	0.30	0.18	-

Figure 4.10. Photo of the peel test specimen of Al-foam/GFPP modified with PP-g-MA

4.1.3. Flexural Properties of Al/GFPP Laminates

Load–displacement curves of Al/GFPP laminates with silane treated, polyolefin based adhesive film incorporated and modified with PP-g-MA film obtained after bending test are presented in Figures 4.11 to 4.13.
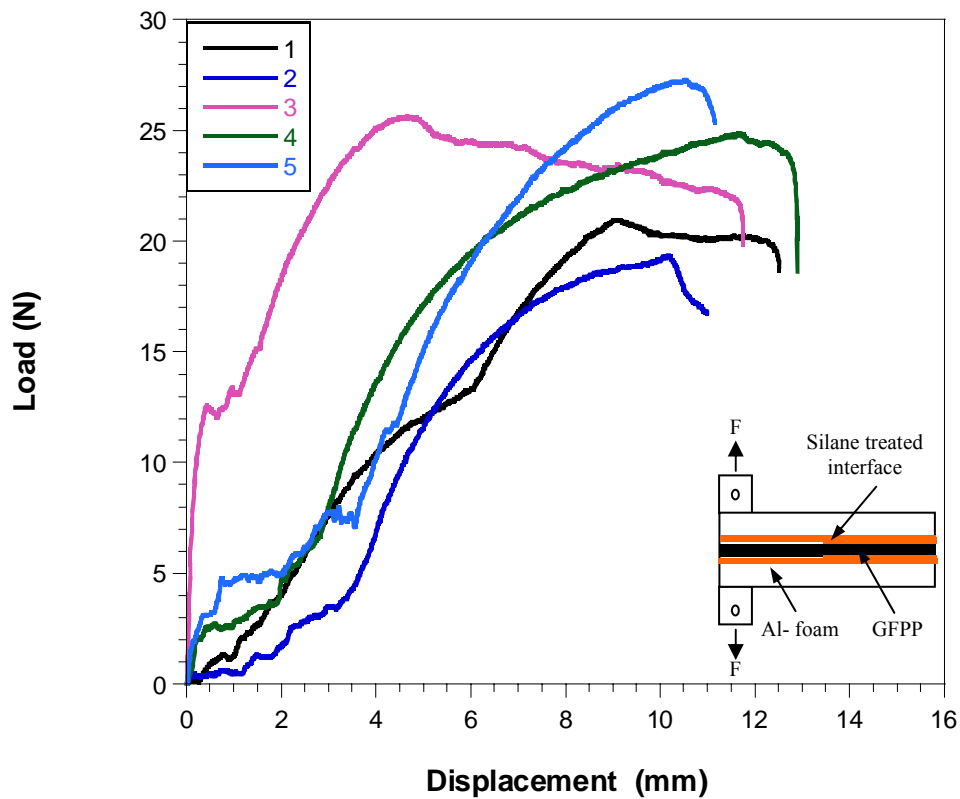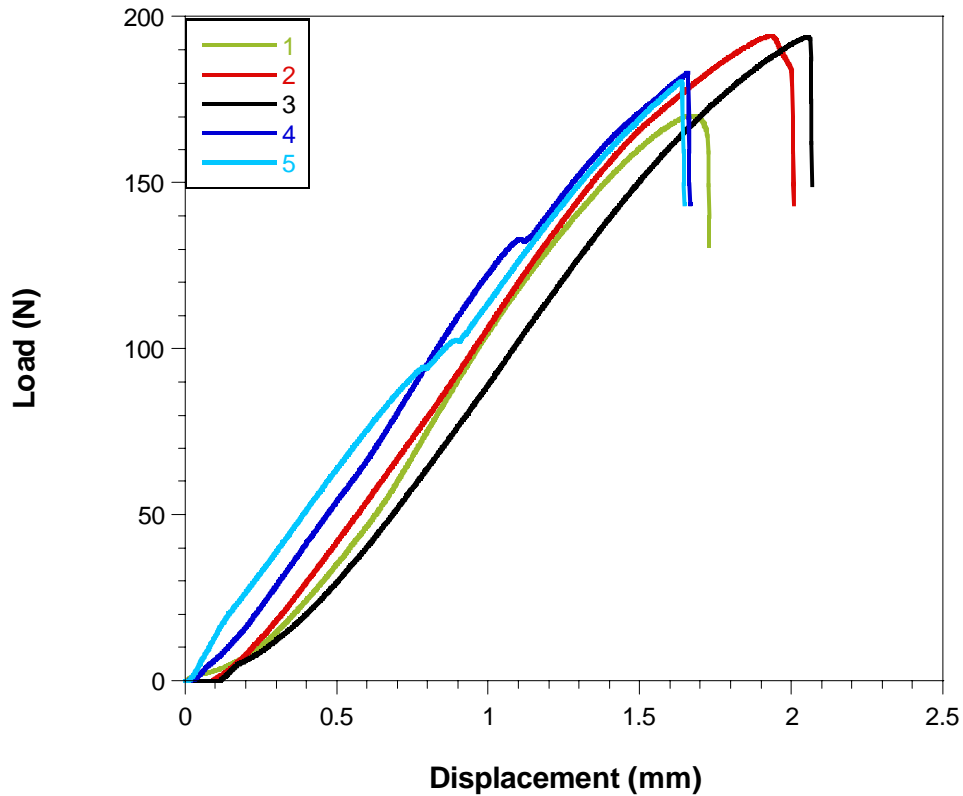

Figure 4.11. Load – displacement graphs obtained after bending test for silane treated Al/GFPP (numbers indicate that five samples tested from the same batch)

As seen in Figure 4.11, for silane treated Al/GFPP, bending loads increases linearly for all of the specimens, and reaches to maximum level at about 2 mm displacement. In the linear region the response is elastic, and failure occurs at the maximum load level. These samples exhibited the lowest bending strength values (27.22-31.07 N/mm^2) as compared to those with other samples. As seen in Figure 4.12, polyolefin based adhesive film incorporated Al/GFPP laminates exhibited similar behaviour with silane treated samples. However, samples with polyolefin based adhesive film exhibited higher flexural strength values at higher displacements as compared to silane treated Al/GFPP specimens . In case of Al/GFPP laminates modified

with PP-g-MA, as seen in Figure 4.13, exhibited no sudden drop of the load and the highest strength values as shown in Table 4.3. This indicates the best adhesion obtained with PP-g-MA modification of the interface of Al/GFPP and interlayer materials exhibits a high level of plastic deformations. The bending strength values of the composites with various interface modifications are tabulated in Table 4.3. Bending strengths were significantly improved to 90.8 N/mm^2 for laminates modified with PP based film containing 20 wt. % PP-g-MA. Carrillo and Cantwell (2009) found the bending strength of thermoplastic matrix fiber metal laminate based on a self reinforced polypropylene composite and Al approximately 160 N/mm^2.
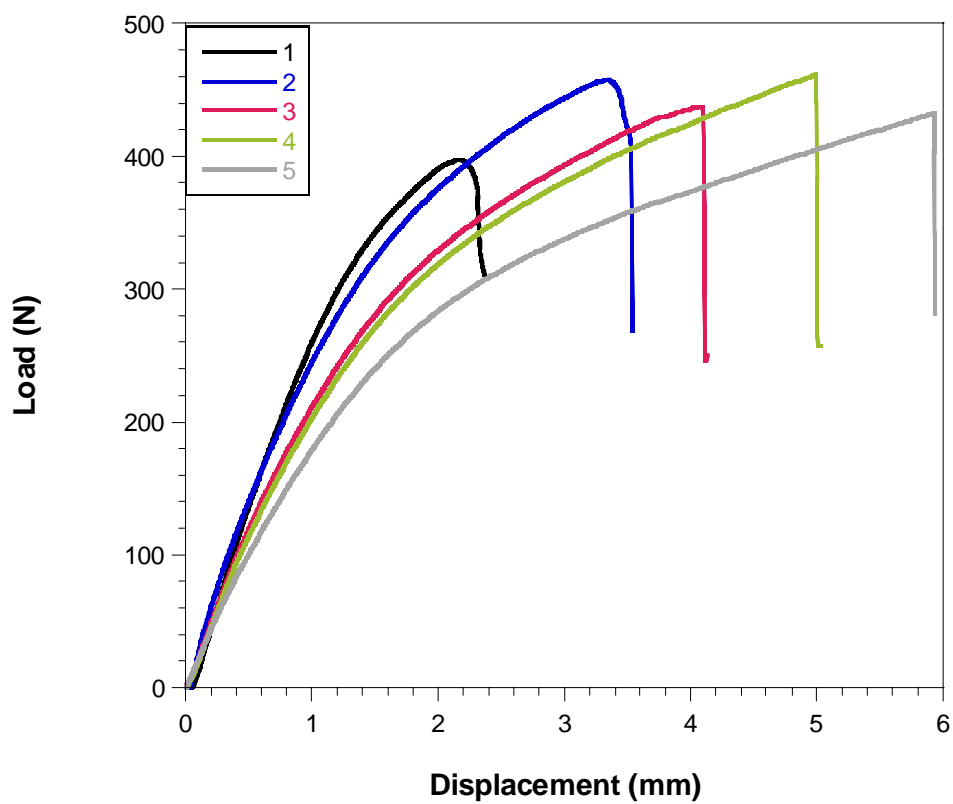
Figure 4.12. Load–displacement graphs obtained after bending test for polyolefin based adhesive film incorporated Al/GFPP (numbers indicate that five samples tested from the same batch)
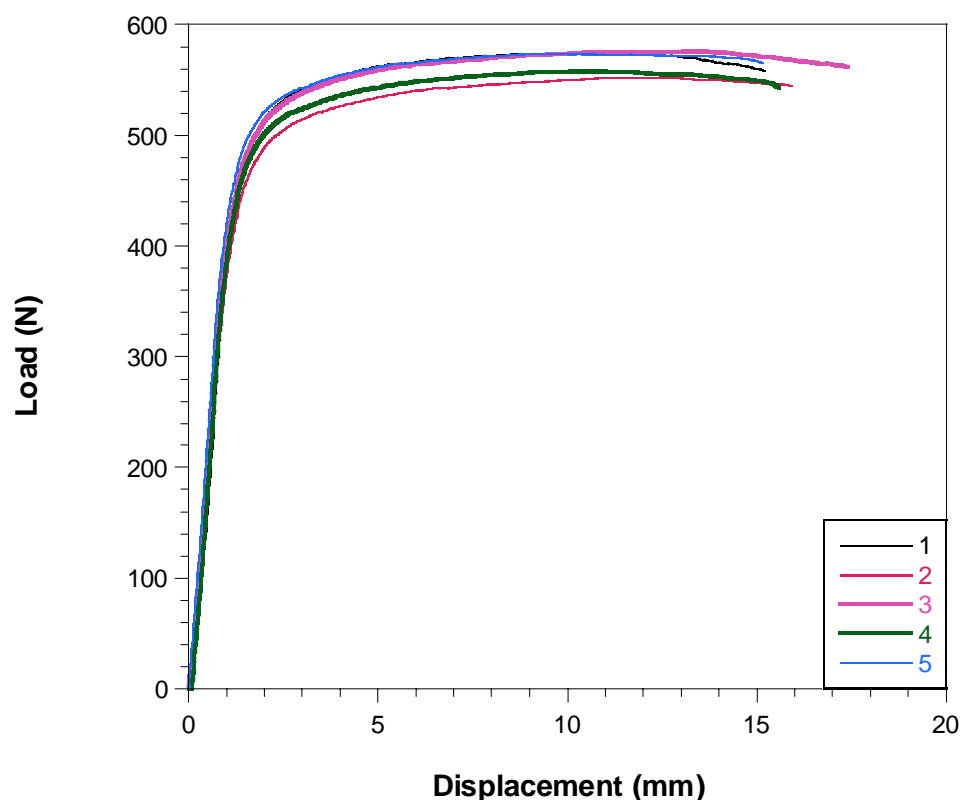
Figure 4.13. Load–displacement graphs obtained after bending test for Al/GFPP modified with PP-g-MA (numbers indicate that five samples tested from the same batch)

Table 4.4. Bending strength values for Al/GFPP laminates with various interface modifications

Sample Al/GFPP	Bending Strength (N/mm^2)			
	Untreated	Silane treated	Polyolefin based adhesive film incorporated	Modified with PP-g-MA
1	No bonding	27.22	63.58	92.07
2	No bonding	31.07	73.20	88.46
3	No bonding	31.03	69.92	92.17
4	No bonding	29.44	73.90	89.29
5	No bonding	28.94	69.22	91.95
Average	**-**	**29.54**	**69.96**	**90.79**
Standard Deviation (+/-)	**-**	1.61	4.10	1.77

The samples deformed during flexural testing are presented in Figure 4.14. As seen in the figure, Al/GFPP laminates modified with PP-g-MA film did not show any delamination or cracking between the layers. However, interlayer cracks can be clearly seen for polyolefin based adhesive film incorporated Al/GFPP laminated structures, as expected. On the other hand, cracks are not visible for silane treated Al/GFPP laminated structures, although the sudden drops during bending occured as seen in Figure 4.10.
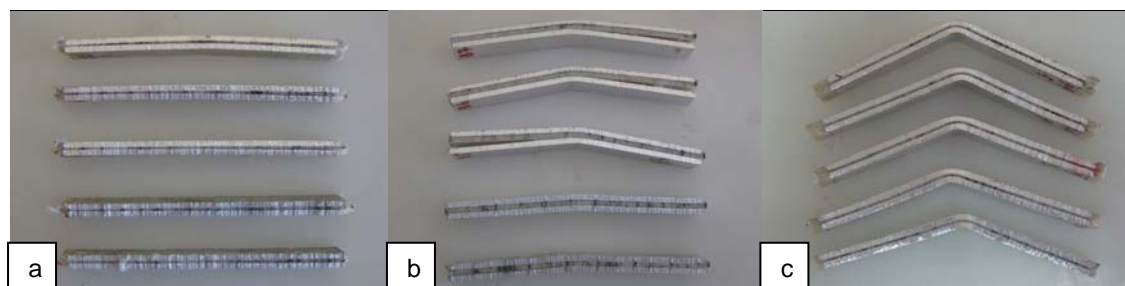
Figure 4.14. Photo of bending samples of Al/GFPP laminated structures a) Silane treated b) polyolefin based adhesive film incorporated c) modified with PP-g-MA

4.2. Microstructure Characterization

ATR-FTIR spectroscopy provided determination of structural groups at the silane treated Al surface. Siloxanes (Si-O-Si) groups formed as the result of the hydrolysis and condensation reactions of silane coupling agents were observed by ATR-FTIR spectroscopy. A strong band due to Si-O stretching vibration occured at 912 cm^{-1} as seen Figure 4.15. Siloxane was characterized by at least one strong band at 1150 cm^{-1} due to asymmetric stretching. The peak at 3550 cm^{-1} is due to the O-H stretching of silanol (Si-OH). The peak at 1650 cm^{-1} is due to C=C stretching of vinyl benzene of the coupling agent. Based on the results, it was concluded that Al surfaces were coated with siloxane layers successfully.

Optical microscopy was used to examine the cross sections of the laminates with different surface pretreatment techniques before mechanical testing. The resulting micrographs were shown in Figure 4.16. Based on the micrographs it was revealed that the corresponding material surfaces bond to each other continously with all surface

pretreatment techniques. No significant defect such as voids and unbounded regions were observed at the interface.
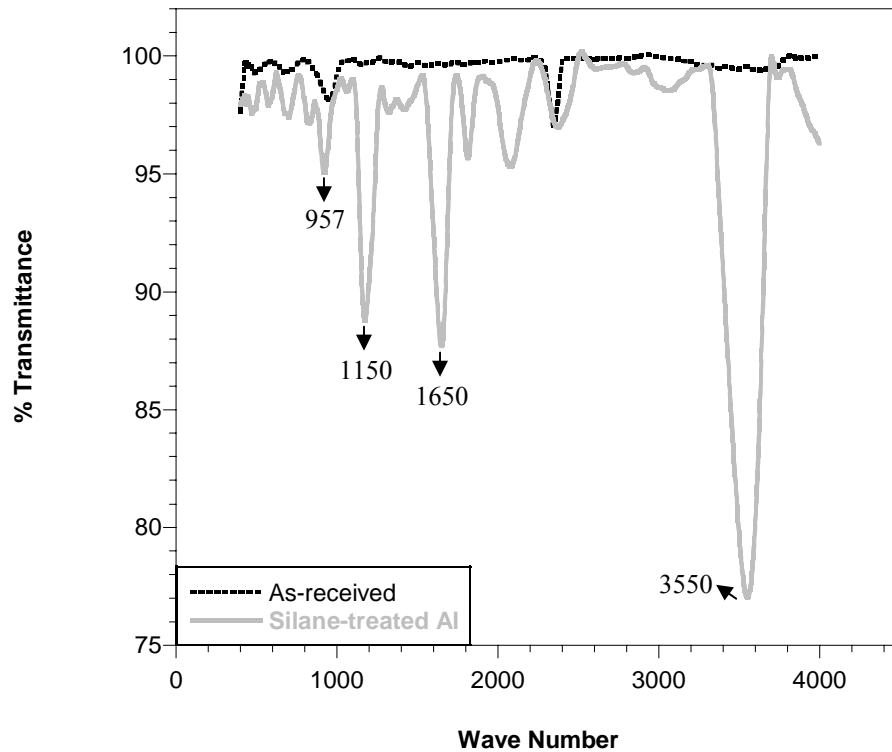
Figure 4.15. ATR-FTIR spectrum of untreated and silane treated Al surfaces
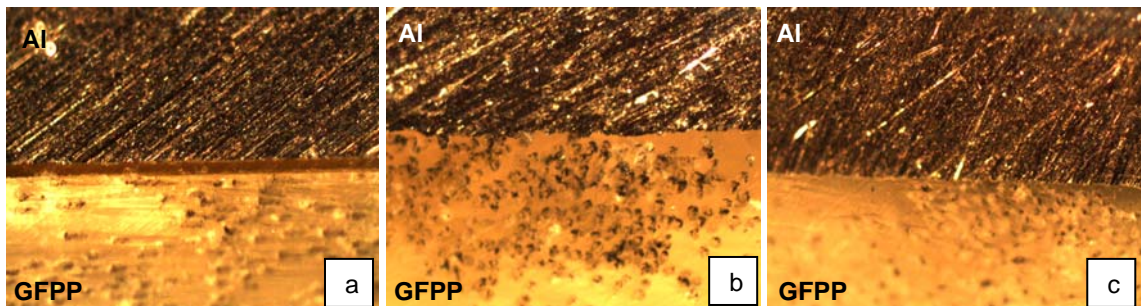
Figure 4.16. Optical micrographs of cross sections of Al / GFPP with a) Silane treated b) polyolefin based adhesive film incorporated c) modification of PP-g-MA structures (20x)

SEM was used to characterize the fracture modes of laminated specimens after lap-shear testing. Figure 4.17 and 4.18 show the fracture surface SEM micrographs of Al/GFPP laminate interface with as-received, silane treated, polyolefin based adhesive film incorporated and modification of PP-g-MA specimens after shear testing. The images are taken from the Al side of the laminate.

For the case of as-received Al, no residual polypropylene was observed on the delaminated Al interface. This is due to no interfacial chemical and physical interactions between PP and the polished Al surface. Chen et al. (2007) also experienced the similar results. In Figure 4.17 (b) polymer matrix material and glass fibers attached on the Al surface is observed for the laminates with silane treatment after shear testing. The presence of polymer composite layer on the metal surface and cohesive failure of the composite layer indicates a relatively good adhesion of metal/GFPP interface. Images at higher magnification (Figure 4.18 (b)) for the same surfaces also shows that deformation around fibers occurs that indicating a higher interfacial strength.

Figure 4.17. Fracture surface SEM images of Al / GFPP with a) As-received b) Silane treated c) polyolefin based adhesive film incorporated d) modification of PP-g-MA structures (80x)

A layer of polymer film was observed on the fracture surface of polyolefin based adhesive film incorporated Al/GFPP interface as seen in Figure 4.17 (c). This indicates the weak failure strength of adhesive film inserted between Al and GFPP interlayer. The same observation can be obtained in Figure 4.18 (c) at higher magnification.

The SEM micrograph of the fractured Al/GFPP interface modified with PP-g-MA is shown in Figure 4.17 (d). As seen in Figure 4.17 (d) glass fiber and polymer matrix remains on the Al surface. The deformation of PP matrix and debonding and pull-out of fibers are very extensive. This indicates that the failure is cohesive through the polymer composite layer. It can be deduced that best adhesion is achieved by PP-g-MA modification. Higher magnification micrograph of the shear fractured surface of is shown in Figure 4.18 (d). As seen in the figure, PP matrix material and glass fibers bond tightly. This also imply the enhanced bonding at the interlayer region and occurance of plastic deformation in the PP layer during lap shear test.
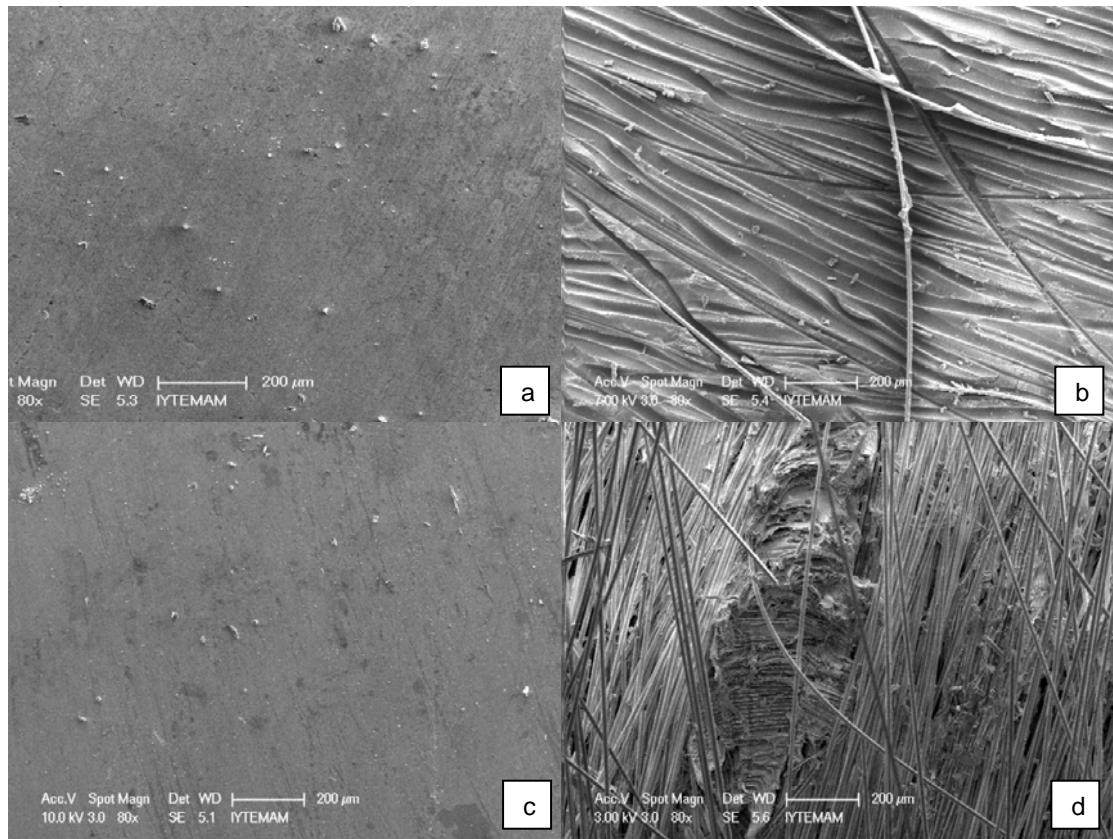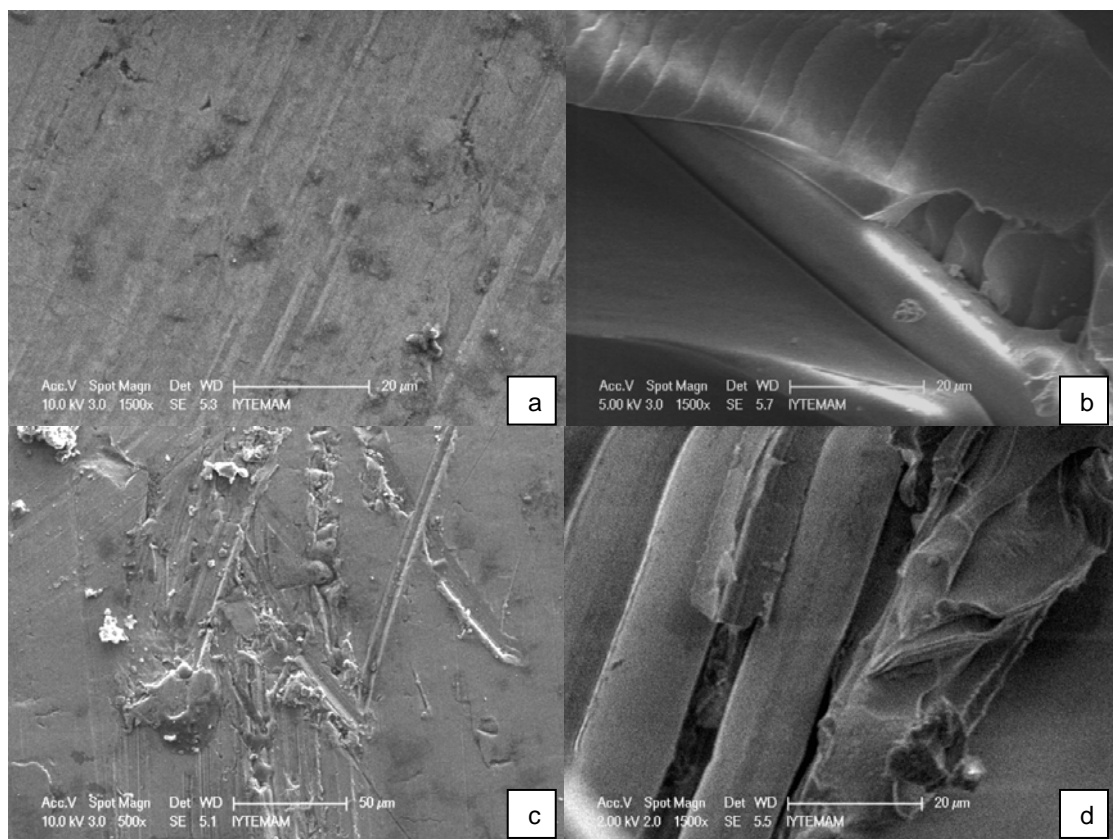

Figure 4.18. Fracture surface SEM images of Al / GFPP with a) As-received b) Silane treated c) polyolefin based adhesive film incorporated d) modification of PP-g-MA structures (1500x)

CHAPTER 5

CONCLUSIONS

In the present study, the effects of various surface modification techniques on the adhesive properties of Al/GFPP laminates were presented. To tailor the interface of Al/GFPP, amino based silane coupling agent that has compatibilty with polypropylene was employed. Another approach was incorporation of polyolefin based adhesive film and PP based film containing 20 wt. % PP-g-MA between Al and GFPP.

Lap-shear, peel and bending strength tests were performed in order to reveal the effects of various surface modification techniques on adhesive properties of Al/GFPP laminates. SEM micrographs of Al/GFPP laminate interface with and without surface modifications after shear testing were obtained to evaluate failure mechanisms.

Untreated Al/GFPP samples exhibited almost no bonding between Al and GFPP. Interfacial shear strength value of 2.03 N/mm^2 was obtained by silane treatment of Al surfaces. It was concluded that amino based silane (Z-6032) provided significant improvement in interfacial shear stresses over the untreated specimens. This improvement was due to the chemical bonding between polypropylene and the amino group of the Z-6032 silane as expected. As compared to the others, polyolefin based adhesive film gave the lowest interfacial shear strength value (0.57 N/mm^2). This may be related with low process temperature of polyolefin based adhesive film (145°C) which is under the melting point of PP (165°C). So no melting on the surface of GFPP during lamination may cause to the poor adhesion. Besides, it is not possible to increase the process temperature of polyolefin based adhesive film (145°C) above the melting temperature of the GFPP (200°C) because polyolefin based adhesive film has a melting point of 66°C and degredation at elevated temperatures occurs. Interfacial shear strength value of Al/GFPP interfaces modified with PP-g-MA was found as 5.93 N/mm^2. It was concluded that the introduction of PP based film containing 20 wt. % PP-g-MA into the Al/GFPP interlayer resulted in substantial improvement of the fracture strength and toughness of the adhesive joint.

Peel strength values were found as zero for untreated Al/GFPP samples indicating no bonding between Al and GFPP. The peel strength values of Al/GFPP silane treated, polyolefin based adhesive film incorporated and modified with PP based film containing 20 wt. % PP-g-MA were increased to 0.53, 2.67, and 6.61 N/mm, respectively. Based on peel strength results, best adhesion was achieved by the introduction of PP based film containing 20 wt. % PP-g-MA into the Al/GFPP interlayer. The peel strength of silane treated Al-foam/GFPP laminate (1.01 N/mm) exhibited two times greater values than those with silane treated Al/GFPP laminate (0.53 N/mm). This may be related with the surface roughness of the Al foams. However, a reduction in peel strength of polyolefin based adhesive film incorporated Al-foam/GFPP laminate (0.91 N/mm) was measured as compared to those with Al layer (2.67 N/mm). For the laminates with PP-g-MA, the peel strength was found to be over 1.75 N/mm. So, due to the best adhesion between Al-foam and GFPP surfaces with PP-g-MA interlayer, peeling at the interface did not occur, but bending of the Al-foam was observed at critical bending stresses. Based on lap-shear strength values of Al/GFPP, incorporation of polyolefin based adhesive film into the Al/GFPP interlayer gave the lowest values. However, according to peel strength values, application of silane was a less effective surface treatment compared with the incorporation of polyolefin based adhesive film. It was concluded that in shear direction silane treated Al surfaces resisted longer than polyolefin based adhesive film incorporated Al surfaces. Besides, strengths of polyolefin based adhesive film incorporated Al/GFPP interfaces were weaker in peel direction.

The bending strengths values of Al/GFPP silane treated, polyolefin based adhesive film incorporated and modified with PP based film containing 20 wt. % PP-g-MA were found as 29.54, 69.96 and 90.79 N/mm, respectively. In case of Al/GFPP laminates modified with PP-g-MA, these laminates exhibited no sudden drop of the load and the highest strength values compared with other surface modification techniques.

The shear, peel and bending strength results clearly indicated that the best adhesion between Al and GFPP composite has been achieved by incorporating PP based film containing 20 wt. % PP-g-MA.

Based on SEM images, it was concluded that there was no interfacial chemical and physical interaction between PP and polished Al surface. By incorporation of polyolefin based adhesive film between Al and GFPP, residual polypropylene on the

fractured surfaces was seen indicating weak interfacial strength of adhesion consistent with the results of lap-shear strength. SEM micrographs for fractured surfaces of silane treated Al/GFPP indicated better adhesion because of the PP layer seen on the surface of the fractured Al. According to the SEM micrographs, it was exhibited that incorporation of PP-g-MA into the Al/GFPP interface provides the highest interfacial adhesion between Al and GFPP.

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