

# Improving Interfacial Adhesion Between Thermoplastic Polyurethane and Copper Foil Using Amino Carboxylic Acids

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**ABSTRACT:** A chemical methodology to improve the adhesion between copper foil and a thermoplastic polyurethane (TPU) matrix is reported. The copper foil (0.127 mm thickness) was treated with aminocarboxylic acid-based coupling agents such as 6-aminohexanoic acid and 4-aminobenzoic acid. 3-Aminopropyl trimethoxysilane was also used as a conventional silane coupling agent for comparative studies. The interfacial adhesion between copper foil and laminated TPU was examined by means of peel adhesion test, scanning electron microscopy, and attenuated total reflection-infrared spectroscopic methods. The

treatment of copper foils with 6-aminohexanoic acid resulted in improved adhesion, which was equal to that of the silane-treated system. The mechanism of how the coupling agents strengthen the interfacial adhesion between TPU and copper foil is discussed. The solution concentrations of the coupling agents were optimized with respect to the peel adhesion of the interface. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1738–1744, 2009

**Key words:** metal-polymer adhesion; polyurethane; coatings; compatibilization; interfaces

## INTRODUCTION

Polymer coatings on metals play a significant role in various technological applications. Two of the most important functions of such coatings are to provide high electrical insulation and to provide protection from environmental damage. Polymer coatings on copper substrates are widely used for insulation and protection of circuit-board, wire, and coils in the electrical and electronic industries.<sup>1–3</sup> The mechanical strength of copper/polymer interfaces is of great importance, as delamination can degrade the performance and reliability of entire electrical systems. The effectiveness of these polymer/metal interfaces can be greatly increased through the use of adhesion-promoting organic coupling agents. When properly formulated and cured, polyurethane coatings combine numerous desirable properties such as toughness, flexibility, high resistance to abrasion, excellent electrical insulating properties, and good moisture and chemical resistance.<sup>4</sup>

Adhesion is a complex phenomenon related to physical effects and chemical reactions at the interfaces between coating materials and metal substrates. Adhesive forces specifically in copper foil/polyurethane systems result as the metal is chemically treated and heated in contact with the polymer films. The magnitude of these forces obviously depends on the nature of the treated copper surfaces and the efficiency of binding with the polyurethane coating. The forces may be broadly categorized as existing as two types: the primary forces corresponding to covalent bonds in the energy range of 15–170 kJ and the secondary forces including hydrogen bonds, dispersion, dipole, and induction forces with a much lower energy in the range of 0.5–12 kJ.<sup>5</sup> All these forces are assumed to participate in the adhesion of polymer coatings such as polyurethane on copper. More generally, adhesion between metals and polymers is known to be a balance between wetting, chemical, or physicochemical bonds formed at the interface and the bulk features of the coating polymers.<sup>6</sup> There have been many research efforts whose goals have been to determine which factors lead to maximum adhesion. In most instances, this work has led to the use of a range of adhesion promoters, and questions as to whether mechanical or chemical interactions control interfacial adhesion.<sup>5–12</sup> Studies of typical adhesion promotion schemes include wet chemical treatments such as oxidizing solution treatments (acidic and alkaline) and electroplating-anodizing schemes.<sup>2,13–16</sup> Surface modifications have

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been attempted by exposure to organic bonding agents as well as dry chemical interactions such as ion implantation and surface alloying.<sup>16–21</sup> Wet chemical treatments have made use of hot alkaline oxidizing treatments with oxidants such as sodium chlorite and hydrogen peroxide.<sup>2,13–16</sup> These treatments generate some baseline level of surface roughness and increase the level of metal surface oxidation. More subtle surface modifications such as ion implantation and organic complexation agents tend to affect the surface chemistry but do not affect the bulk topography.<sup>16–21</sup> Kim et al.<sup>22</sup> have studied the interfacial adhesion of amine and hydroxyl functionalized polystyrene with copper, and they found significant improvement of adhesion of polystyrene with copper.

In this work, the adhesion of thermoplastic polyurethane (TPU) on copper foils has been characterized. The role of adhesion promoters and a new molecular-scale mechanism is proposed and discussed. Although a significant literature is already dedicated to polymer-metal interfacial adhesion, details of polyurethane/copper adhesion enhanced by aminocarboxylic acid-based coupling agents has not been described previously to the best of our knowledge. The results of several adhesion promoters and processing variations were investigated both in terms of macroscopic adhesion and molecular bonding.

## EXPERIMENTAL

### Materials

Copper foils (thickness 0.127 mm; Alloy 110 Electronic-Grade) were obtained from McMaster-Carr (Los Angeles, CA) 6-Aminohexanoic acid (99+%), 4-aminobenzoic acid (99%), and 3-aminopropyl trimethoxysilane were obtained from Sigma-Aldrich (Milwaukee, WI). Polyether-based thermoplastic polyurethane (ESTANE 58315 TPU, Noveon, Wickliffe, OH) was used as received. Ethyl alcohol (95%) USP was supplied by Aapper Alcohol (Chatham, Ontario).

### Method of chemical treatments

3-Aminopropyl trimethoxysilane and 6-aminohexanoic acid solutions in water (0.25, 1, 5, and 10 wt %) were applied to copper foils. The copper strips (2 cm × 15 cm) were immersed into the warm aqueous chemical solutions (70 mL, 80–85°C) for the indicated times (1, 24, and 72 h). A 100-mL borosilicate test tube was used for the chemical treatment. The copper strips were treated with different concentration of 4-aminobenzoic acid solution in ethyl alcohol (0.25, 1, 5, and 10 wt %) at room temperature for 1, 24, and 72 h. The excess chemical compatibilizers were removed by washing with either water or ethanol, and then the treated copper strips were dried at 50°C for 2 h using a vacuum oven.

### Preparation of TPU-coated copper foils

TPU films (~ 2 mm thickness) were prepared from TPU pellets using a Carver model C press (Wabash, IN) at 190°C. Next, untreated and chemically treated copper foils were coated with TPU films using the same hot press at temperature of 190°C, pressure of 5 MPa, and press times of 5, 30, and 60 min. A thin poly (tetrafluoroethylene) film (0.13 mm) was inserted between the ends of the TPU and copper foils to facilitate the delamination during peel tests.

### Adhesion measurements

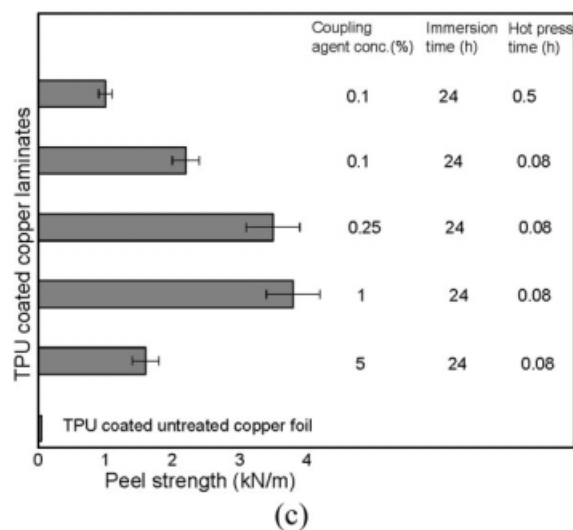
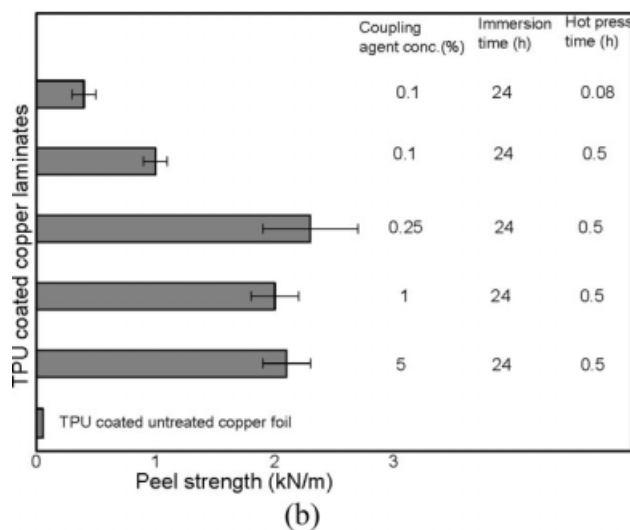
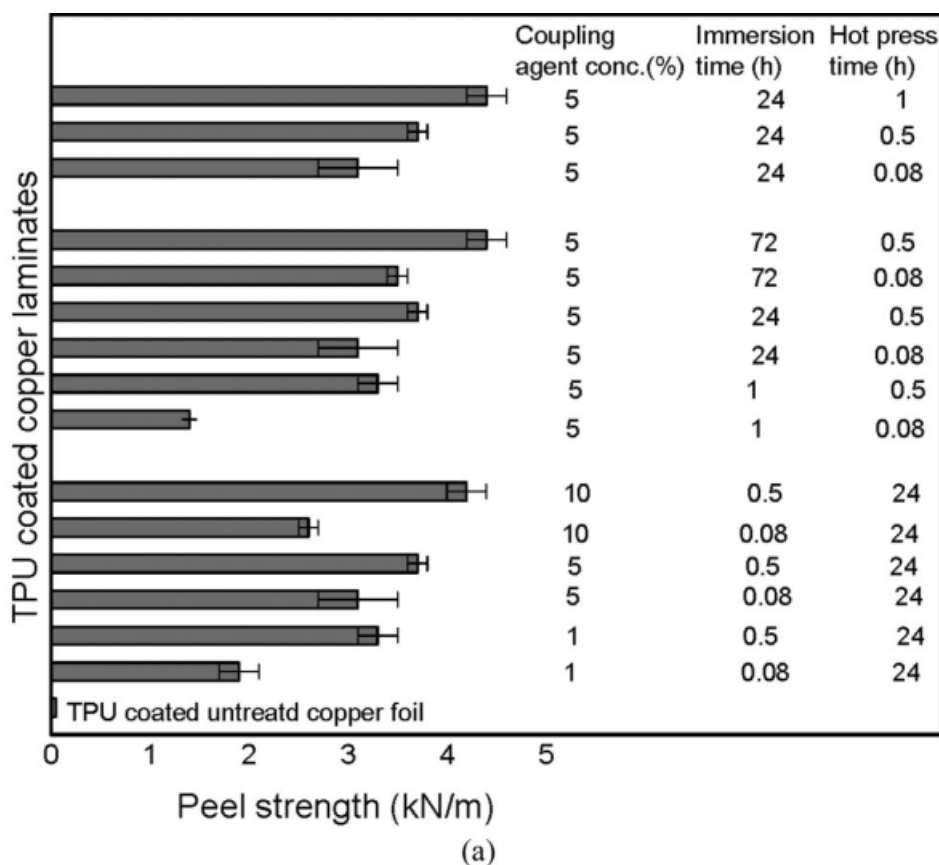
The peel test is a widely used method for determination of polymer-metal interfacial adhesion.<sup>9,10</sup> The adhesion peel strength of the TPU-coated copper foils were examined according to ASTM Standard D903-2004 using an Instron model 5565 universal testing machine at an extension of 100 mm/min. Each sample of coated foil was tested five times with five prepared specimens; averaged results and standard deviations are reported.

### Scanning electron microscopic (SEM) studies

The copper foils were cut into small pieces (average length and width, 0.2–0.4 mm) and mixed with TPU matrix using a DACA model 2000 twin-screw corotating microcompounder (Santa Barbara, CA). The blending of 10 wt % copper foils (chemically treated and untreated) with TPU was carried out at 100 rpm screw speed, blending for 5 min at 190°C, and then isothermally heated at 190°C for 25 min prior to extrusion. The wetting characteristics of copper foils with TPU matrix were investigated by analyzing SEM photomicrographs of the samples taken at 10 kV using a Phillips XL 30 ESEM scanning electron microscope (SEM) (Carbridge, UK). The copper particle-filled extruded samples were cryogenically fractured and coated with palladium and then exposed surfaces were analyzed by SEM.

### Attenuated total reflection-infrared spectroscopy (ATR-IR) studies

The surfaces of the untreated and chemically treated of copper foils were analyzed before coating by using attenuated total reflection-infrared (ATR-IR) techniques. Similarly, the failure surfaces of both copper foils and TPU films were also characterized by ATR-IR method to analyze the functionalities playing the role in improving the adhesion between copper foil and TPU film. The ATR-IR spectra were taken using MIRacle™ ATR (manufactured by PIKE Technologies, Madison, WI) using a zinc selenide ATR crystal.



**Figure 1** (a) Effect of 6-amino hexanoic acid on peel strength of TPU-coated copper foils. (b) Effect of 4-amino benzoic acid on peel strength of TPU-coated copper foils. (c) Effect of 3-aminopropyl trimethoxy silane on peel strength of TPU-coated copper foils.

## RESULTS AND DISCUSSION

### Adhesion peel test

The adhesion characteristics of the TPU-coated copper foils were studied by evaluation of peel strength. The peel strength values of TPU-coated copper foils are illustrated in Figure 1(a), wherein the copper foils were treated with aqueous solutions of 6-amino-

hexanoic acid under different conditions. The untreated copper foil/TPU laminate showed average peel strength of  $<0.05$  kN/m. There was a dramatic increase of adhesion peel strength while copper foils were treated with 6-aminohexanoic acid (1, 5, and 10% aqueous solution). Figure 1(a) further shows that the optimum peel strength was obtained when at least 5% aqueous solutions were applied to the

copper foils. The results show that the peel strength is a function of hot press time, and peel strength increases with increasing hot press time. The optimum peel strength ( $\sim 4.4$  kN/m) was obtained by increasing either press time or immersion time of copper foil in aqueous solution of 3-aminohexanoic acid. There was a moderate increase of peel strength of copper foil/TPU laminate when copper foil was treated with alcohol solutions of 4-aminobenzoic acid [Fig. 1(b)]. The optimized peel strength (2.3 kN/m) of copper foil/TPU was achieved at 0.25% concentration of 4-aminobenzoic acid in ethanol; there was no significant change of peel strength at higher-concentration (i.e., 1 or 5%) of 4-aminobenzoic acid.

The conventional, commercial silane coupling agent (3-aminopropyltrimethoxy silane) produced TPU/Cu laminates with an optimized adhesion peel strength of 4.4 kN/m [Fig. 1(c)]. Treatment under mild concentration (0.25–1 wt %) of aqueous silane solution resulted optimum peel strength of the laminates. The advantages of the silane solution was that it needed less hot press time when compared to that with the aminocarboxylic-based coupling agents. It is reported elsewhere that 100% surface coverage is not possible for most substances due to steric interactions and crowding due to the size of the coupling agent molecules.<sup>23,24</sup> In the present investigation, it is observed that the 0.25–1 wt % (0.014–0.056M solution) silane coupling agent and 5 wt % (0.38M solution) 6-aminohexanoic acid produce laminates with same level of peel strength (with maximum value of 4.4 kN/m). 4-aminobenzoic acid produces maximum level (2.3 kN/m) of peel strength at concentration of 0.25 wt % (0.019M solution). The results suggest that the silane coupling agent is more reactive than amino carboxylic acids. The silane agent contains three hydrolysable methoxy groups in its molecular structure, whereas each amino carboxylic acid contains one functional acid capable of interacting with the urethane linkages of the TPU. The more modest effect of 4-aminobenzoic acid with Cu/TPU on peel strength is possibly due to the large steric bulk of its phenyl rings, limiting surface coverage.

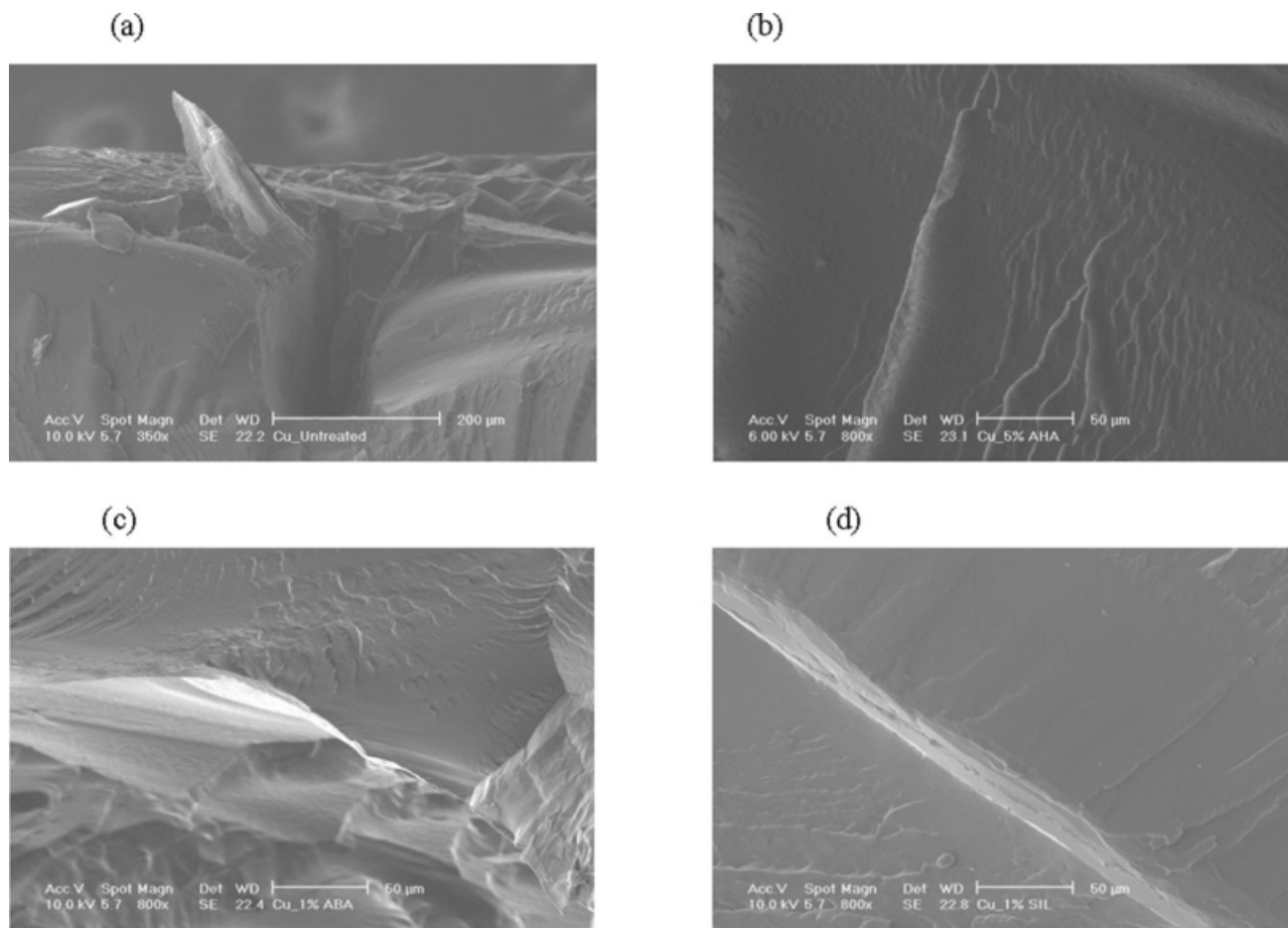
### Scanning electron microscopic studies

Interfacial adhesion can be assessed qualitatively through SEM fractography studies (Fig. 2). To understand the copper-TPU matrix adhesion, the cryogenically fractured surfaces of extruded TPU/copper flake composites (containing 10 wt % Cu particles) were studied using SEM. The cryogenically fractured surface of the composite with untreated Cu is shown in Figure 2(a), and it reveals that the Cu particles are pulled out of the composite and the holes left after Cu particle pull-out are clean.

The proximal ends of the extracted Cu particles buried in the matrix with poor sticking between metal and the matrix. This observation indicates the poor interfacial adhesion between the untreated Cu foil/particle and the TPU matrix. The SEM microphotographs of the cryogenically fractured surfaces of the TPU composites with Cu particles treated with 5 wt % (0.38M solution) 6-aminohexanoic acid, 1 wt % (0.07M solution) 4-aminobenzoic acid, and 1 wt % (0.056M solution) 3-aminopropyl trimethoxy-silane solutions are shown in Figure 2(b–d), respectively. The proximal ends of the Cu particles are buried in the matrix with good adhesion between the metal and matrix. A number of river structures are also observed on the fracture surfaces of the composites, indicating that large amount of energy was absorbed and dissipated through shearing of the polyurethane matrix during the fracture process. This accounts for higher observed interfacial adhesion properties of the TPU with Cu particles treated with different organic coupling agents. Good adhesion between the Cu particles and polymer matrix results in efficient stress transfer from the continuous polymer matrix to the dispersed Cu particles and can increase the ability of the material to absorb energy.

### ATR-IR spectral analysis

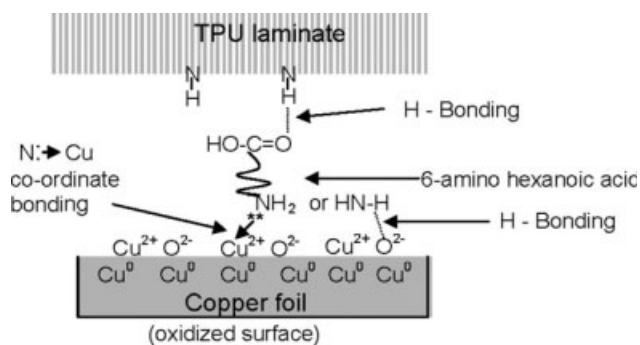
Near the interface with the metal, the polymer microstructure may differ from its equilibrium bulk configuration due to the interactions with the metal and the restrictions that it imposes on the mobility of the polymer chains. The nature of chemical species at the interface and of the conformations of the polymeric coating in the region near the interface is an important aspect to arrive at understanding of the ultimate delamination behavior of polymer-metal laminates. The oxidation of copper is very fast in an air atmosphere.<sup>11,12</sup> Hence, it is very difficult to observe a pure Cu surface. The main oxide types on the Cu surface are CuO, Cu<sub>2</sub>O, Cu(OH), and Cu(OH)<sub>2</sub>. The Cu<sub>2</sub>O oxide is converted to CuO by a slower oxidation process in air. The formation of oxides on Cu surfaces is enhanced when the temperature is increased. It is reported in literature that, the thermal aging of copper foil at relatively high temperature affects not only the coating structure but also the copper-polymer coating interface by enhancing the oxidation process on the copper surface.<sup>25</sup> Moreover, the formation of a low cohesion Cu<sub>2</sub>O and CuO layer at the copper/polymer interface is assumed to strongly influence the adhesion strength.<sup>25,26</sup> The adhesion of copper/polymer interface broadly depends on the role of adhesion promoter, copper oxidation, and thermal aging in the adhesion mechanism.



**Figure 2** SEM photomicrographs of the cryogenically fractured TPU/10 wt % Cu composites: (a) Cu, untreated, (b) Cu, treated with aqueous solution of 5 wt % 6-amino hexanoic acid, (c) Cu, treated with ethanol solution of 1 wt % 4-amino benzoic acid, and (d) Cu, treated with aqueous solution of 1 wt % 3-aminopropyl trimethoxy silane.

The ATR-IR spectra of the untreated control copper foil and TPU film, and the peeled-copper foil and TPU film, where the treatment of 6-amino hexanoic acid was applied prior to lamination were all taken. The treated peeled-TPU film exhibited similar IR characteristics of untreated TPU film. The peeled-copper foil showed the presence of characteristic polyurethane IR peaks. The untreated and treated peeled-TPU films showed broad and weak IR bands around  $3300\text{--}3340\text{ cm}^{-1}$ , which may be assigned to the merging of IR bands of H-bonded and free N—H groups of TPU film,<sup>27,28</sup> but the copper foil showed a sharp and weak band at  $3300\text{ cm}^{-1}$ , which corresponds to H-bonded N—H group; the free N—H band is absent on the peeled-copper foil, implying that the polyurethane moiety is bonded to the copper foil using the free N—H group as hydrogen bonded through the coupling agent (6-amino hexanoic acid) (Fig. 3); as the peeled-copper foils did not show any IR band associated with free N—H group. The pure TPU and peeled-TPU films along with the peeled-copper foil showed two C=O stretching band at  $1725\text{ cm}^{-1}$  (free) and  $1701\text{ cm}^{-1}$  (hydrogen

bonded).<sup>29</sup> The peak at around  $1700\text{ cm}^{-1}$  mainly arising from the hydrogen bonding of NH (urea, amide, or urethane) to carbonyl groups (urethane), whereas free stretching vibration appears at about  $1725\text{ cm}^{-1}$ . A third weak C=O band was observed at about  $1640\text{ cm}^{-1}$  on the untreated TPU and peeled-copper foil (peeled-TPU film did not show



**Figure 3** Proposed reaction mechanism of 6-amino hexanoic acid as a compatibilizing agent between copper foil and TPU matrix.

this band), which may be assigned to the stretching vibration of hydrogen bonded urea or amide carbonyl.<sup>29</sup> The IR band at  $1640\text{ cm}^{-1}$  was stronger on the peeled-copper foil surfaces, presumably due to the formation of more amide groups by the reaction between carboxylic acid group from 6-aminobenzoic acid and N—H groups from polyurethane at high temperature ( $190^\circ\text{C}$ ). Thus from the ATR-IR analysis, it is proposed that some of the N—H groups of polyurethane are attached to the coupling agent (6-aminohexanoic acid) via hydrogen bonding and other N—H groups form amide linkages.

The ATR-IR spectra of the peeled-copper foils and TPU films where the samples were treated with 4-amino benzoic acid were also taken. The peeled-copper foils exhibited characteristic IR bands of polyurethane (such as C=O stretching at about  $1725$ ,  $1700\text{ cm}^{-1}$ ), as was the case with 6-aminohexanoic acid-treated samples. Both pure and peeled-TPU films showed a weak broad band from  $3300$  to  $3340\text{ cm}^{-1}$ , which is assigned to the free and hydrogen bonded N—H groups of polyurethane. Peeled-copper foils exhibited IR band at  $3240$  and  $3120\text{ cm}^{-1}$ , which may be ascribed to the free and hydrogen bonded N—H groups of 4-amino benzoic acid. The peeled-TPU film also showed a band at about  $3240$  and  $3120\text{ cm}^{-1}$ . The ATR-IR spectra of the peeled-copper foil and TPU films, where silane coupling agent (3-aminopropyl trimethoxy silane) was used as an adhesion promoter, were also obtained. The pure TPU and peeled-TPU exhibited similar ATR-IR bands, except the weak band at about  $1640\text{ cm}^{-1}$ , which may be due to the presence of C=O stretching of urea or amide groups, was absent on the peeled-TPU film. The peeled-copper foil also showed some characteristics IR peak of polyurethane, such as C=O stretching at  $1725\text{ cm}^{-1}$  (free) and  $1700\text{ cm}^{-1}$  (hydrogen bonded). Many researchers have reported that the adhesion strength between polymer and metal could be enhanced significantly by incorporation of nitrogen- or oxygen-containing functionalities into the polymer<sup>30–32</sup>; but this hypothesis is contradicted by the polyurethane/Cu system. Further, chemical treatment of Cu with amino acids or silane solution appeared to be necessary to reach desirable adhesion strength. Many researchers in the field of biochemistry have reported that the strong coordination bonding of amino acids to transition metals occurring via a chelate binding mode involving both carboxylate and amine groups.<sup>33–36</sup> Thus, there exists a possibility that the free carbonyl group of the chelated carboxylate of 6-aminohexanoic acid may be assigned to bond TPU through H-bonding with free —NH group of polyurethane. There are some reports about interfacial activity of a nitrogen- or oxygen-containing functionality onto metal surfaces<sup>37–40</sup> and it was reported that OH groups are more effective

than  $\text{NH}_2$  groups in enhancing the adhesion strength between polystyrene and copper.<sup>22,23</sup> It may be hypothesized that the carboxylate group of amino carboxylic acids coordinate with Cu, whereas the amino end is hydrogen-bonded to polyurethane. The formation of copper chelate complexes may be possible only with 6-aminohexanoic acid; the steric factor may not permit the formation of copper chelate complex with 4-aminobenzoic acid.

## CONCLUSIONS

The amino carboxylic acid based coupling agents improve the interfacial adhesion of Cu/TPU laminates dramatically. The untreated Cu/TPU laminate shows effectively no adhesion (peel strength,  $0$ – $0.5\text{ kN/m}$ ). The chemical treatment of Cu foil with 4-amino benzoic acid and 6-amino hexanoic acid improve the peel strength values to average values of  $2.3$  and  $4.4\text{ kN/m}$ , respectively. The average peel strength of Cu/TPU is  $4.4\text{ kN/m}$ , whereas 3-aminopropyl trimethoxysilane is used. The lower peel strength of 4-aminobenzoic acid-treated Cu/TPU laminate than 6-aminohexanoic acid treated one is presumably due to steric hindrance created by benzene ring. The silane agent applied contains three hydrolysable methoxy groups, which most likely increases the reaction kinetics and subsequently produces Cu/TPU laminate with optimum adhesion strength at minimum hot pressing time and aqueous concentration of silane coupling agent when compared with amino acids. The SEM photomicrographs also reveal very strong interfacial adhesion between chemically treated Cu and TPU matrix. It is assumed from the literature<sup>22,23,33–40</sup> and the ATR-IR spectra presented herein that the free amino groups of the TPU are H-bonded to free carbonyl group of the chelated copper carboxylate of 6-aminohexanoic acid; there is another possibility that the acid group of amino carboxylic acids coordinate with Cu and amino ends are hydrogen-bonded to polyurethane. Finally, it may be concluded that 6-aminohexanoic acid has the potential to replace the conventional silane coupling agent for improving interfacial adhesion between copper and TPU matrices.

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