

Effect of Metal Particle Incorporation on Adhesive and Electrical Properties of Acetylene-Terminated Polyisoimide Prepolymers

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Synopsis

Modification of properties of an addition-curing polyisoimide prepolymer is achieved by the incorporation of small metal particles. No evidence for the modification of the cure chemistry of the prepolymer is observed. Physical modification of the system is observed in electrical, dynamic mechanical, and adhesive properties. Compositions containing various volume fractions of metal and polymer were prepared. Two different molecular weights of prepolymer were studied. Samples were prepared by fabricating single overlap adhesive specimens to aluminum. These lap shear specimens were then used for the electrical and adhesive properties of the material. The electrical properties improved markedly at above 25 volume percent metal loading. The adhesive properties to aluminum showed a maximum at 20–25 volume percent loading. X-ray photoelectron spectroscopy was used to examine adhesive failure surfaces.

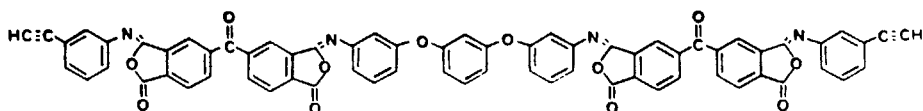
INTRODUCTION

The improved processibility that has been demonstrated¹ in addition-cured polyisoimide systems allows more utilization of the already excellent thermal and mechanical properties available in polyimide systems. Furthermore, the range of properties available in these materials may be extended significantly by the combination of heterogeneous fillers such as metal particles. These polymer/metal composites would exhibit a unique combination of properties which could extend the utility of polymeric materials. For example, in most polymer-metal composite systems, the heat distortion temperature and stiffness increase while the thermal expansion coefficient, tensile modulus, and impact strength decrease.² Another interesting effect observed is in the area of electrical conductivity. At a critical volume loading of metal filler the electrical conductivity of the composite increases dramatically.³ These observations have prompted our investigation of the chemistry and properties of an acetylene-terminated polyisoimide prepolymer matrix (Fig. 1) filled with an aluminum/nickel (1 : 1) alloy powder.

EXPERIMENTAL

Fourier transform infrared spectrometry (FTIR) was performed on a Nicolet 6000 Infrared Spectrometer. Spectra were obtained at 4 cm⁻¹ resolution and

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IP-600

Fig. 1. Structure of acetylene-terminated polyisoimide prepolymer: Thermid IP-600.

were the average of at least 10 scans. Neat polymer samples were prepared by casting on a KBr window from a 5%(w/w) solution of the polymer in tetrahydrofuran (THF). The solvent was removed by vacuum drying at 60°C. FTIR cure experiments were carried out using a Barnes Model C019-020 heated cell. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-4 at a heating rate of 10°C/min with a nitrogen purge. Thermogravimetry (TG) was performed on a Perkin Elmer TGS-2 thermogravimetric analyzer at 10°C/min in a dynamic air atmosphere with a purge rate of 50 mL/min. Dynamic mechanical thermal analysis (DMTA) was performed on a Polymer Laboratories DMTA Mechanical Spectrometer in the single cantilever mode at a frequency of 1 Hz and a heating rate of 5°C/min between 0°C and 300°C. Electrical properties were measured using Keithly instrumentation. Scanning electron microscopy (SEM) was performed on a Phillips Scanning Transmission Electron Microscope. Thermid IP-630 and IP-600 were obtained from National Starch and Chemical Corporation (Bridgewater, NJ). Aluminum/nickel (1:1) alloy powders were provided by Alcoa Corporation. Samples were prepared for testing by compression molding a well-mixed powder mixture at room temperature followed by curing at 220°C under moderate pressures (< 100 psi).

RESULTS AND DISCUSSION

Previous work conducted in our laboratory has focused on the thermal crosslinking and isomerization reactions occurring in polyisoimide prepolymer systems. We have also investigated the electrical properties of metal-filled polyisoimides at elevated temperatures when used for bonding aluminum conductor bars. During this study it was observed that qualitatively good adhesion was achieved with aluminum substrates. This observation prompted the study described herein which focuses on the dynamic mechanical, adhesive, and electrical properties of these systems.

As mentioned previously, FTIR spectrometry has been used in conjunction with DSC to establish the contributions of isomerization and crosslinking to the overall curing reaction of the neat polyisoimide. The presence of small, oxide-coated metal particles in this matrix, however, may influence these reactions. Unfortunately, obtaining high-quality FTIR spectra of this metal-filled system has been difficult. The data that have been obtained do not seem to indicate any influence of the metal powder on the reactions which occur during cure. This observation is further supported by the appearance of the DSC thermogram (Fig. 2) comparing the neat polyisoimide (IP630) with a 25% (v/v) alloy-polyisoimide composite (MPC). In this study, the weight of metal

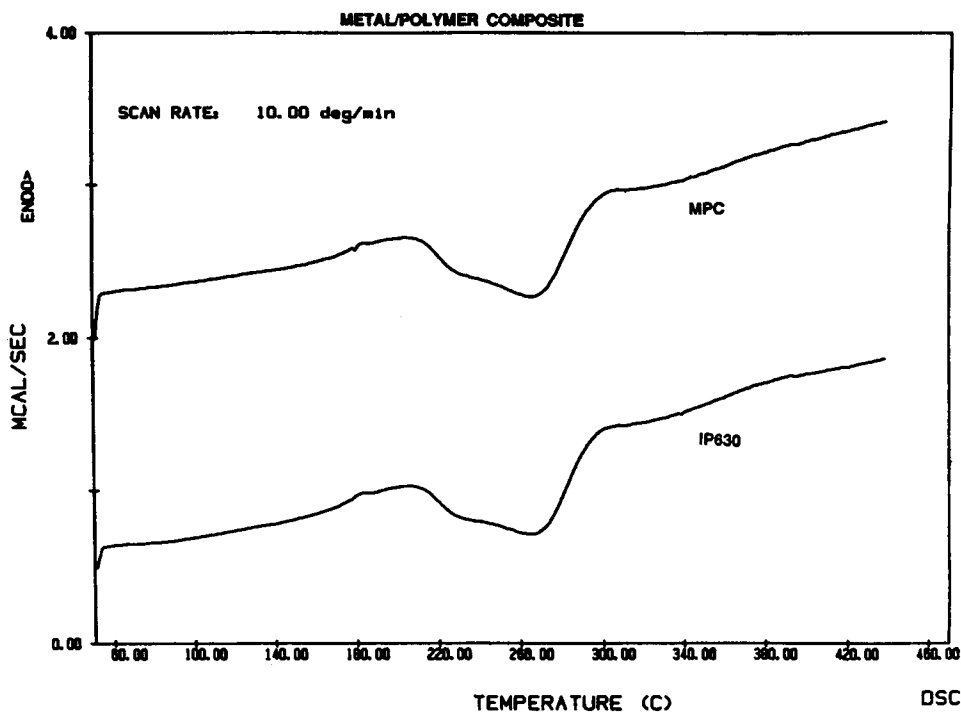


Fig. 2. Comparison of DSC thermograms of neat IP-630 and a 25% (v/v) metal-containing metal-polymer composite.

was subtracted out so that the peak areas could be measured in energy per gram of polymer. The similarity of thermograms for the neat and filled polymer as well as the energies of reaction derived therefrom further suggest that the metal powder does not interact chemically with the polyisoimide during cure.

Although these data do not indicate any chemical interaction of the metal with the polymer, physical interactions occurring in these systems do give rise to modification of dynamic mechanical, electrical, and adhesive properties.¹⁻⁴ It is thought that these property modifications result from a combination of factors such as (1) large-scale interactions of polymer chains with the metal particles, (2) interactions between the metal particles themselves, and (3) interactions of both the polymer and metal powders with the surface of the adherends.

Changes in both the damping and modulus-temperature behavior have been noted. Specifically, the mechanical behavior as a function of temperature was measured for both a neat, cured film of Thermid IP-630 isoimide prepolymer with a number average molecular weight of $\sim 17,000$ and a metal/polymer composite consisting of 5% (v/v) aluminum/nickel (1:1) alloy in a matrix of the same prepolymer. Both materials were cured at the same temperature and pressure. The $\tan \delta$ relative damping spectra of these two materials are compared in Figure 3. Most apparent are the broadening of the main damping peak (i.e., glass transition, T_g) and also the appearance of a post T_g dispersion

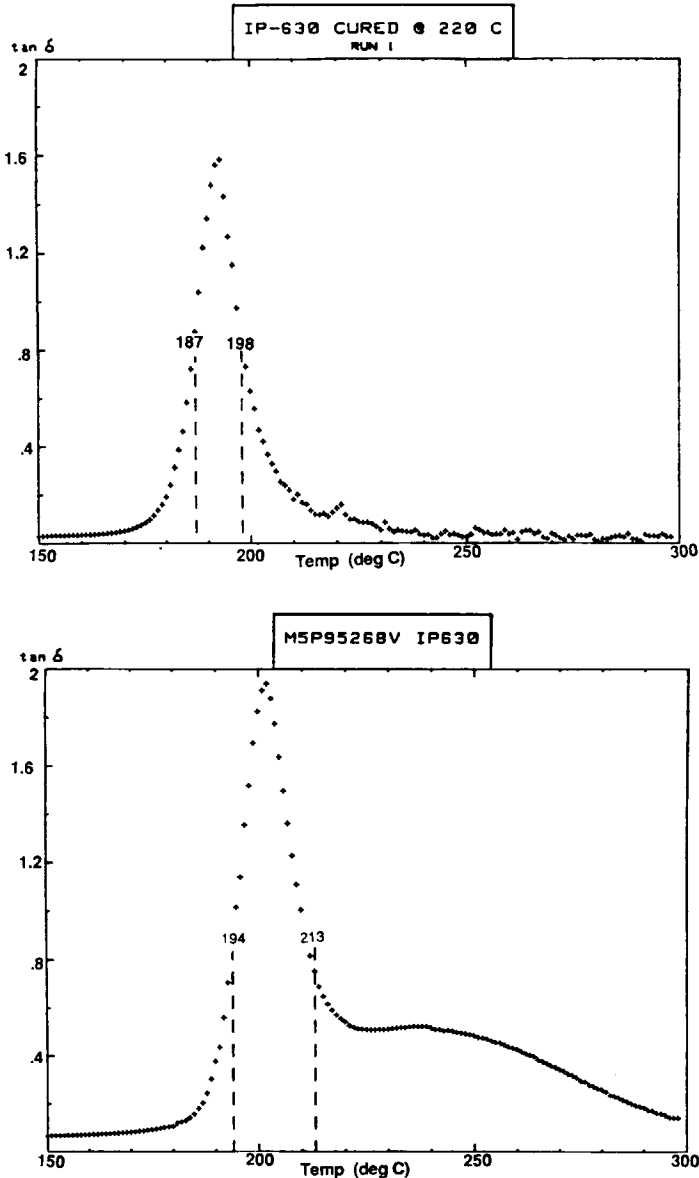


Fig. 3. Comparison of damping peaks for neat IP-630 and a 5% (v/v) metal-containing metal-polymer composite.

for the case of the metal/polymer composite. These two effects are presumably due to the greater potential dissipation of mechanical energy through frictional losses caused by the polymer segments moving across the surfaces of the metal particles. This reasoning would also explain the slightly larger magnitude of the $\tan \delta$ peak for the case of the metal/polymer composite. Modulus temperature behavior is modified by the reinforcing effect of the filler particles in the polymer matrix.

Since the $\tan \delta$ spectrum represents the ratio of the loss (E'') to storage (E') modulus, it is also instructive to examine these dynamic mechanical

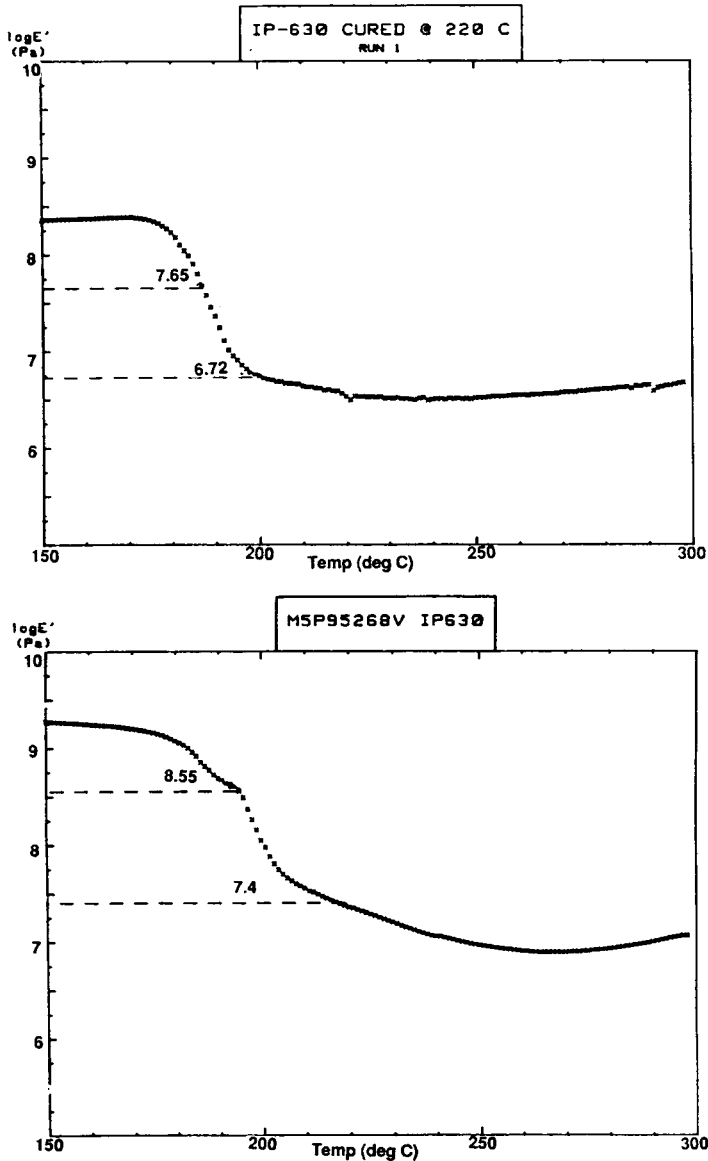


Fig. 4. Comparison of the storage moduli of neat IP-630 and a 5% (v/v) metal-containing metal-polymer composite.

spectra as well. Although there are no distinct differences apparent in the shapes of the two loss modulus curves, an examination of the storage modulus curves provided some explanation regarding differences in the $\tan \delta$ plots. The reinforcing effects of the filler are expected to be more apparent in the storage modulus behavior (Fig. 4). It must be noted, however, that the absolute values of the modulus data quoted here are not significant since absolute calibration was not performed. What can be used as a basis for comparison in this study is the difference in modulus values between the temperature limits which correspond to the breadth of the $\tan \delta$ peak at one-half of its maximum value. This comparison shows that the metal/polymer composite storage modulus

(E') decreases by a greater magnitude over this temperature range than does the E' value for the neat polymer (1.15 log units for the MPC versus 0.97 log units for the neat polymer). This observation can be explained on the basis of the reinforcing efficiency of the filler being diminished as the matrix proceeds from the vitrified to the rubbery state at the glass transition temperature.

The modification of electrical properties that occurs in MPC has been described in terms of percolation theory and is due to physical interaction among the metal particles themselves. At room temperature the electrical properties of these composites are governed almost exclusively by the volume fraction, size, shape, and distribution of the conductive metal particles in the composite. In the present case the data suggest that these materials behave as randomly dispersed composites (i.e., metal particles distributed in a random fashion) in contrast to a segregated composite. In the latter the filler particles are preferentially distributed at the interfaces where the initial polymer particles were sintered together during cure.⁵ Scanning electron microscopy has been used to characterize the shape and size of the particles; while, the densities of each component (metal and polymer) were used to calculate the volume loading. SEM analysis of the particles showed randomly shaped particles with no characteristic dimension. These particles were 20-70 μm in diameter and were assumed to approximate spheres. The percolation threshold for conductivity based upon our assumptions of particle shape and size is predicted to be above 30% (v/v) loading of metal particles.

The data obtained for two different molecular weight prepolymers (IP600, $M_n \sim 1100$; IP630, $M_n \sim 17,000$) in terms of both the actual lap shear joint resistance and also the calculated volume resistivity (ρ_v) are shown in Tables I and II. At low loading levels the resistivity of the polymer dominates, and no current flow is measured through the sample. As the loading of metal is increased, the resistivity begins to drop gradually until, at some critical loading level, the resistivity drops precipitously by ~ 3 orders of magnitude. This sudden drop marks the volume loading which is considered the percolation threshold for conduction.

These data suggest that in the case of the lower molecular weight material, IP600, the resistivity decreases at a lower volume percent loading than in the

TABLE I
Volume Percent Metal Loading versus Resistance for 0.5 in²
Single Lap Shear Joints on Aluminum^a

Percent loading (v/v) metal/polymer IP600	Resistance	ρ_v ohm-cm
50/50	0.7 m Ω	3.7×10^{-2}
25/75	6.3 m Ω	0.73
20/80	6.2 m Ω	0.72
15/85	0.09 Ω	10.4
10/90	0.15 Ω	17.3
5/95	—	$> 1.2 \times 10^{4b}$
0/100	—	$> 1.2 \times 10^{4b}$

^aBond thicknesses ranged from 8-14 mils except for 50/50 case where bond thickness ranged from 21-27 mils.

^bLess than 0.1 amp current flow at 24 volt load.

TABLE II
Volume Percent Metal Loading versus Resistance for 0.5 in²
Single Lap Shear Joints on Aluminum^a

Percent loading (v/v) metal/polymer IP630	Resistance	ρ_v ohm-cm
50/50 ^b	1.6 m Ω	9.0×10^{-1}
25/75	0.9 Ω	1.0×10^2
20/80	2.1 Ω	2.4×10^2
15/85	—	$> 1.2 \times 10^{4b}$
10/90	—	$> 1.2 \times 10^{4b}$
5/95	—	$> 1.2 \times 10^{4b}$
0/100	—	$> 1.2 \times 10^{4b}$

^aBond thicknesses ranged from 9–13 mils except for 50/50 case where bond thickness ranged from 21–24 mils.

^bLess than 0.1 amp current flow at 24 volt load.

case of the higher molecular weight, IP630, material. This result may be due to several influences. First, since the IP600 has lower molecular weight, it would be expected to have a lower melt viscosity prior to gelation. This lower viscosity could lead to greater effective pressure on the bonds during cure. The greater effective pressure could be responsible for more metal-metal contact between the aluminum adherends and the metal particles present in the adhesive layer.⁶ Also, since these are acetylene-terminated materials the lower molecular weight system would result in a more densely crosslinked network which would help to maintain contact during cooldown and subsequent vitrification of the material.

Another aspect of these materials which has been investigated is the mechanical response, in terms of lap shear strength to aluminum, as a function of metal loading. Again, two different molecular weight prepolymers were employed. The lap shear data as a function of metal loading are shown in Tables III and IV for the IP600 and IP630 materials, respectively. In both cases a maximum in lap shear strength occurs at a particular loading level. In the case of the lower molecular weight prepolymer this maximum is observed at 15–20% (v/v) loading; while, in the higher molecular weight system the

TABLE III
Effect of Volume Percent Metal Loading on Lap Shear Strength^a

Sample (v/v) percent metal/polymer (IP600)	Lap shear strength (psi)
50/50	700 \pm 100
25/75	940 \pm 80
20/80	1100 \pm 50
15/85	1120 \pm 20
10/90	850 \pm 30
5/95	750 \pm 60
0/100	950 \pm 60

^aBonds were cured at 220°C for 1 h under 500 psi pressure, aluminum adherends. Error limits were calculated from duplicate measurements on at least three samples.

TABLE IV
Effect of Volume Percent Metal Loading on Lap Shear Strength^a

Sample (v/v) percent metal/polymer (IP630)	Lap shear strength (psi)
50/50	600 ± 150
25/75	1600 ± 40
20/80	1300 ± 150
15/85	1300 ± 110
10/90	1450 ± 150
5/95	1350 ± 80
0/100	1430 ± 130

^aBonds were cured at 220°C for 1 h under 500 psi pressure, aluminum adherends. Error limits calculated from duplicate measurements on at least three samples.

maximum occurs at 25% (v/v) loading. This maximum is presumably due primarily to changes in the compliance of the composite adhesive as a function of metal loading. Another factor which may contribute, however, is the interfacial strength between the composite adhesive and the aluminum adherends. This contribution may be important, since in all cases a mixed mode of failure is observed where both adhesive and cohesive debonding occur. It should also be noted that no optimization of bonding conditions was attempted. Conditions were chosen arbitrarily to insure comparability of samples. The potential strengths of these materials would thus be expected to be greater than those quoted here.

In all cases (but to varying degrees) deformation of the aluminum adherends occurs. The deformation that occurs is the bending of the bonded area of the adherends with respect to the line of force during the tensile test. This bending results in a dramatic increase in the peel forces at the edges of the bondline. Failure then occurs by propagation of a crack at the interface between the adhesive and adherend until the crack reaches the central region of the bond. The crack then propagates through the adhesive for a short distance; it then proceeds to the other interface and propagates to failure.

Upon visual inspection of the bond, three regions are apparent (Fig. 5). Region 1 is comprised of polymer with a lustrous coating of metal oxide. This region corresponds to region 3 of the opposite adherend; in this region a clean oxide surface of the adherend is observed. Region 2 contains polymer on both adherends and is slightly narrower than either of the other regions. The X-ray photoelectron spectroscopy (XPS) samples which are described next have been taken from region 1.

In order to better understand this failure process X-ray photoelectron spectroscopy (XPS) was used to examine the failure surfaces of several bonds. Table V shows the XPS data for two bonds prepared with IP630 prepolymer and either 5 or 25% (v/v) loading of metal. Also shown in this table are the lap shear strengths and the atomic concentrations of three elements which can be used to identify various components of the system. Nitrogen, which is present only in the polymer can provide a tag for the concentration of the polymer at the polymer-rich failure surface (Region 1, Fig. 5). In both cases the surface is almost entirely carbon, since the atomic concentration of

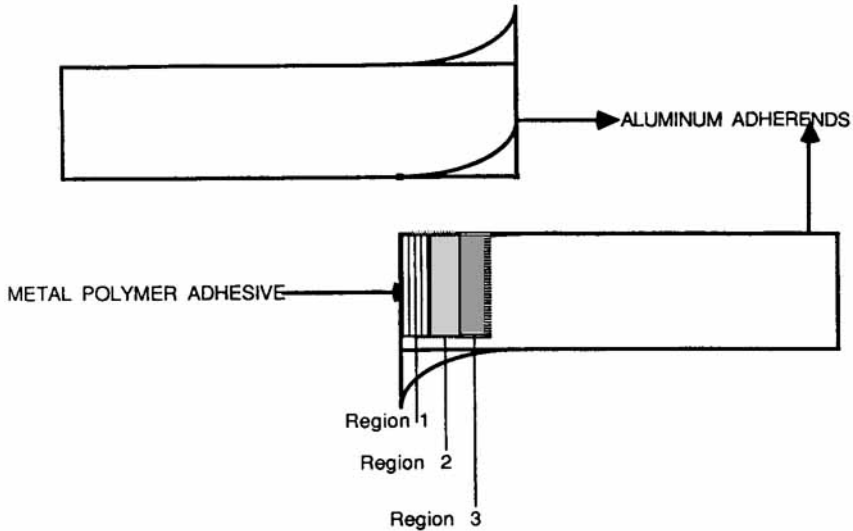


Fig. 5. Schematic of failed aluminum lap shear coupon illustrating the bending of the adherends and different failure regions.

nitrogen in the pure polyimide is calculated to be 4.7%. A significant amount of aluminum is also present due either to the filler particles or to the oxide surface of the adherend. Nickel is present only in the filler particles and would serve as a tag to determine what fraction of the surface is exposed filler particles. However, XPS analysis of the particles alone shows nickel at only 1.3 atomic % due to the large amount of aluminum and oxygen which comprise the majority of the particle surface. The carbon and oxygen signals were also monitored, but were not used in the analysis because of the varying chemical environments in which these elements are present. What does appear in these data is a trend to suggest that the stronger bond, consisting of 25% (v/v) metal filler, has more aluminum and less polymer on the fracture surface than the weaker bond with 5% (v/v) metal. The amount of aluminum in the stronger bond is almost three times that present in the weaker bond (4.28 at.% vs 1.52 at.%). Only a small amount of nickel is observed in the stronger bond (0.20 at.%), indicating that most of the additional aluminum present in this

TABLE V
XPS Analysis of Failure Surfaces^a

Sample (v/v) metal/polymer (IP630)	Element	Atomic %	Lap shear strength (psi)
5/95	N	4.57	1350 ± 80
	Al	1.52	
	Ni	0.00	
25/75	N	3.68	1600 ± 40
	Al	4.28	
	Ni	0.20	

^aBroad oxygen peaks detected indicating both organic and oxide type oxygen.

case is due to the aluminum oxide surface of the adherend rather than more exposed filler particles. The amount of nitrogen in this stronger bond is also decreased, indicating less polymer at the failure surface. These data indicate that in the case of the 5% (v/v) loaded system, the failure in this region is primarily at the interface between the polymer and the adherend; while, in the case of the 25% (v/v) bond the failure occurs more within the aluminum oxide/aluminum metal interface.

The surface pretreatment of the aluminum surfaces in this study was quite simplistic, which undoubtedly affects the measured bond strengths as well as the failure mechanisms. The abrasion of the aluminum surfaces with sandpaper is obviously not the optimal surface pretreatment in terms of bond strength or stability, but it does have the advantage of simplicity. Also, since the study involved measurement of electrical properties of the matrix, most other pretreatment procedures, such as acid etch or anodization, which rely on forming uniform and rather thick oxide layers on the aluminum, would lead to less favorable conductivity through the bond.

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