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Development of Polyaniline/Epoxy Composite as a Prospective Solder Replacement Material

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In this paper we present a novel application of a conducting polymer, polyaniline, as a conductive filler for the development of isotropically conductive adhesives. We have developed isotropically conductive adhesives using protonic acid-doped polyaniline as the conducting filler in an anhydride-cured epoxy system. Fundamental material characterization like DSC, TGA and SEM of the samples was conducted to study their properties. Conductivity of these materials was measured by the four probe method while impact properties were studied by lap shear and drop tests. Samples were aged at 85°C/~100% RH for more than 500 h and the effects of aging were studied. Conductivity value of 10^{-3} S/cm was obtained at 25% PANI filler concentration. These results demonstrate the potential of such systems to function as isotropically conductive adhesives.

Keywords conductive adhesives, polymer composite materials, solder replacement

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INTRODUCTION

Due to the growing concern over the toxicity of lead and its ill effects on the environment, there is a strong consensus globally that lead must be eliminated from electronics packaging and component interconnects. Isotropic conductive adhesives (ICAs) have recently received a lot of attention from researchers in the electronics industry as a potential substitute for lead-bearing solders. ICAs are essentially a certain group of materials which contain insulating polymer matrices and conductive filler, and can simultaneously establish mechanical and electrical joints between the printed circuit board and the surface mount components. ICAs offer non-directional conductivity by incorporating higher filler concentrations [1]. Numerous studies have shown that ICAs possess many advantages over conventional soldering such as environment friendliness, finer pitch printing, and lower temperature processing. Continued efforts in the last 15 years have resulted in the development of ICAs with improved properties, but some of the concerns and limitations are still present. Two major drawbacks of ICAs are poor impact performance and increase in contact resistance under elevated temperature and humidity. Since ICAs mostly use metals as a conductive filler, there is an increase in joint resistance due to corrosion [2].

The primary focus of this work is to develop ICAs with improved properties by using an intrinsically conducting polymer, i.e., polyaniline as the conductive filler. Since most ICAs are essentially a metal in a polymer system, there is a phase barrier which decreases the impact performance. Also, metal surfaces of the filler are susceptible to adverse chemical effects of the matrix. Once the interconnections are established there is a strong possibility of galvanic corrosion due to the presence of two dissimilar metal surfaces. Hence, replacing metallic filler by polymeric filler eliminates these limitations and improves the overall performance of the ICA.

Electrically conducting polymers have conjugated π electron backbones and hence show conducting properties. Composites of conducting polymers are promising materials for various applications, such as rechargeable batteries, electromagnetic shielding, antistatic formulations, sensors, and electronic devices. Among conducting polymers, polyaniline (PANI) is one of the most promising electrically conducting polymers owing to its high polymerization yield, good environmental stability combined with moderate electrical conductivity and low cost [3,4]. Blending PANI with epoxy resin is a good method for developing conducting thermosetting composites with important properties such as antistatic properties, electromagnetic shielding, and anticorrosive properties [5]. PANI salts as conductive filler exhibit many advantages compared to traditional fillers like metals, metallic oxides, and carbon black. Smoother percolation curves can be obtained, compared to the abrupt changes observed, and so the desired electrical conductivity can be tailored. PANI salts have usually low

densities, and therefore conductive composites with low densities can be produced. Also, such composites are all polymeric systems, as both matrix and conductive filler are polymers [6]. Despite such important advantages, there are very few reports in the literature related to epoxy/PANI systems. Peltola et al. [7] prepared electrically conductive adhesive by incorporating PANI doped with camphor-sulfonic-acid into an epoxy resin blend and curing with a Lewis acid. The conductivities obtained were in the antistatic range with less than 2 wt% of conductive salt. Yang et al. [8] reported an alternative approach to conductive epoxy resin/PANI composites with oligomeric PANI in an emeraldine base form followed by doping of the cured films in an acetic acid solution of *p*-toluene sulfonic acid. Although films with high conductivity were obtained, they could not establish a specific use for the product. Electrically conductive adhesives were prepared using commercial dodecylbenzenesulfonic acid (DBSA)-doped PANI as a conducting filler by Pietila et al. [9]. They used methacrylate/acrylate monomers cured by UV radiation. Although an appreciable conductivity level was reported, the impact properties were poor.

The present paper describes the development of epoxy resin/PANI composites as ICAs. PANI was produced by simple chemical polymerization with hydrochloric acid (HCl) as a dopant. A conductivity level of 10^{-3} S/cm was achieved with a PANI concentration of 25%. The impact properties of the ICAs have been studied and the effect of aging due to elevated temperature and humidity were studied. ICAs with better impact properties and stability were developed.

EXPERIMENTAL

Materials

Epoxy resin used was Epon-862 which is based on diglycidyl ether of bisphenol-F (DGEBF), manufactured by Shell Chemical Company, and was purchased from Miller Stephenson Chemical Company, USA. The epoxy equivalent weight of the epoxy is approximately 170 g/equivalent. Anhydride hardener hexahydrophthalic anhydride (HHPA) and the catalyst, 2-ethyl-4-methylimidazole (2E4MZ) were obtained from Sigma Aldrich. Aniline and HCl were supplied by CDH Chemicals, India, while ammonium persulphate (APS) was purchased from Merck India and used as received.

PREPARATION OF ICAs

Formulation of Resins

The resins for the ICAs were formulated as per the following procedure:

- a. The curing agent (HHPA), which is solid at room temperature, was heated slightly to melt it. An appropriate quantity of resin and hardener was added in a ratio of 1:0.85.

- b. The mixture was stirred by a glass rod with heat, if necessary, until a homogenous solution was formed.
- c. After the solution cooled down to room temperature, a certain amount of 2E4MZ, i.e., 0.1 parts per hundred parts of epoxy resin, was added and mixed thoroughly.

Synthesis of PANI

Chemical polymerization of aniline was done by the single step method [10]. A solution of freshly distilled aniline (0.2 M) was prepared in 1 M HCl. The solution was cooled to 0–4°C and an aqueous solution of APS (0.2 M) in Millipore water was added dropwise under constant stirring for 4–5 h. A dark green precipitate is obtained on the filter paper after filtration. It was washed by deionized water several times, dried, and ground into fine powder.

Preparation of ICAs

Different amounts of PANI were added to known amounts of resin and hand-mixed thoroughly to obtain ICAs with 5, 10, 15, 20, and 25% PANI concentration. The conductive filler concentration is described as weight percent.

CHARACTERIZATION

Curing Behavior

Curing behavior of the ICA samples was studied using a differential scanning calorimeter (DSC) from TA Instruments, model Q20. Dynamic scans were done on samples of about 10 mg, at a heating rate of 5°C/min from room temperature to 250°C. Freshly mixed samples were placed in an aluminium hermetic DSC pan and heated under a nitrogen purge. After dynamic scan, samples were cooled to room temperature and scanned again at the same rate. The glass transition temperature (T_g) of the samples was thus obtained.

Thermogravimetric Analysis (TGA)

TGA thermograms of the polymer samples were recorded using a TA Instruments TGA Q50 in the presence of nitrogen up to 600°C at a heating rate of 10°C/min.

Conductivity Measurement

Conductivity was measured by four-probe technique on cured films of the ICAs. The procedure for laying films of the ICAs as already mentioned in our

previous work was as follows [11]. Two parallel strips of tape 5 mm apart were placed along the length of a clean standard glass slide. A small amount of test ICA was placed in the space between the tape strips. Using a square glass cover slip held at a 45° angle, the adhesive was squeezed into the space. The cover slip rides on the tape and provides a uniform film of the adhesive. The tape was removed and the glass slides were placed in a 150°C preheated oven for 1 h. After cure, the samples were dipped in acetone for 2–3 h till solvent swelling occurs and peeled off the glass slide using a doctor's blade. The films were dried in an oven and kept for one day before the conductivity test. Conductivity was measured by means of the standard in-line four-probe method using a Keithley 4200 instrument. The two surfaces of the films were scratched using flint paper before measurements to ensure proper contact. An average of 12 measurements was taken.

Impact Performance

Drop tests were conducted based on the standard established by the National Centre of Manufacturing Sciences (NCMS), USA as per procedure reported earlier [12]. In this test, a mounted chip carrier and circuit board assembly is dropped onto a hard surface from a height of 1.5 m (60 in) and it is necessary for a conductive adhesive to pass six drops for application as a solder replacement.

Moisture Absorption

Moisture absorption tests were performed on bulk samples by conditioning at 85°C/~100% RH until 500 h. Five samples of each adhesive were laid on a glass cover slip having dimensions 80 × 80 mm and cured for 1 h at 150°C in a preheated oven. The cured samples were weighed on a Metler balance (AE-240) and placed on a plastic mesh above the water level in a temperature-controlled water bath. Selected samples were periodically removed and weighed at aging times. The water bath was maintained at 85°C and tightly closed except when samples were removed for testing so that the relative humidity in the water bath chamber was nearly 100%. Unfortunately, no attempt was made to determine whether moisture equilibrium was achieved [13].

Lap Shear Strength Test

Lap shear determines the shear strength of adhesives for bonding materials. The test method is primarily comparative. The test is applicable for determining adhesive strengths, surface preparation parameters, and adhesive environmental durability. The lap shear test was performed as per ASTM D3163 specifications. Two specimens with polyimide material on one side

and copper surface on the other and dimensions of 1" × 4" are bonded together with adhesive so that the overlap area is 1" × 1". The overlap area was etched by flint paper prior to bonding with the adhesive to be tested. The adhesive was applied between etched panels and clamped in place. Thickness was maintained using end strands of a lead wire of diameter 0.1 mm. After curing, cooled specimens were pulled apart by an Electronic Universal Testing Machine (UTM), Instron 3369 at a pull rate of 0.05 in/min. Two groups of specimens were prepared. In each group five samples were prepared for every kind of ICA. One group was tested after cure, the second was tested after conditioning for 500 h at 85°C/~100% RH.

Scanning Electron Microscopy

Scanning electron micrographs (SEM) were obtained with a Zeiss EVO series scanning electron microscope model EVO50 at an acceleration voltage of 10 kV. All samples were plasma-coated with a thin layer of gold to provide electrical conduction and reduce surface charging.

RESULTS AND DISCUSSION

Curing Behavior

DSC is a useful tool to investigate the curing profile of epoxy resin, both neat and when blended. Figure 1 shows the typical DSC thermograms of neat

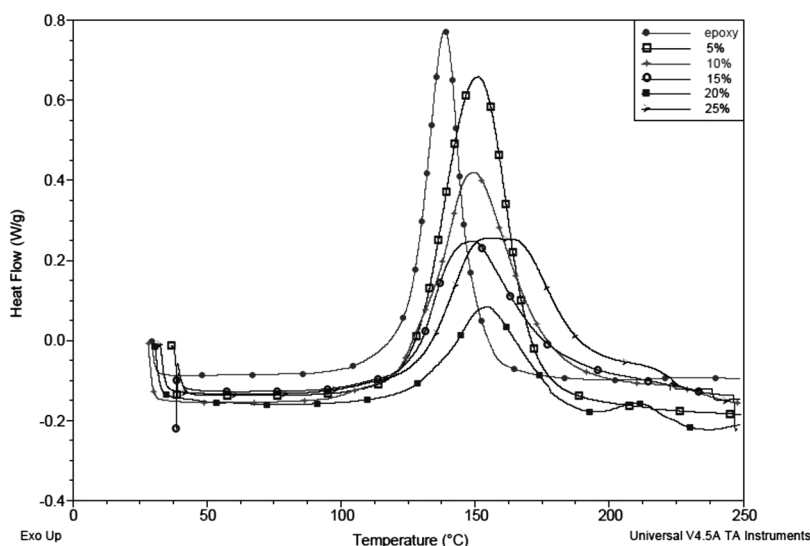


Figure 1: DSC thermograms of epoxy resin and epoxy/PANI composites.

epoxy/anhydride system and that of ICAs with different concentrations of PANI filler. The exothermic peak of the epoxy/anhydride system appears at 138°C, depicting the complete crosslinking reaction of the epoxy system. A single exothermic peak is observed for different concentrations of PANI in an epoxy matrix, indicating that the basic curing profile of the epoxy system is not affected by the addition of PANI. It is observed that with the increase in concentration of PANI in the ICAs, the peak maximum is slightly shifted to higher temperature and also the curing time is increased as indicated by widening of the peak. This may be attributed to the fact that with the increase in PANI concentration, epoxy concentration decreases proportionately, i.e., the percentage of cured component is decreased. The results are in accordance with observations of Tsotra et al. [6]. ICA with PANI concentration of 25% shows a flattening of peak and higher ΔH value. This concentration was difficult to mix as there was a drastic increase in viscosity and the mixture became dry. It may be concluded that the percentage of cured component falls beyond an optimum level and the influence of PANI over the curing process becomes highly significant.

Glass transition values for the ICAs were determined by heating the cured samples up to 250°C (Figure 2). The T_g value of the neat epoxy system was found to be around 115°C. Interestingly, even a 5% PANI concentration has a visible effect on the T_g value as depicted in Figure 2. Similarly, incorporation of higher amount of PANI in an epoxy matrix leads to a significant reduction of T_g values, indicating that the quality of the crosslinked network is substantially influenced. It is observed from the overall cure behavior of the ICAs

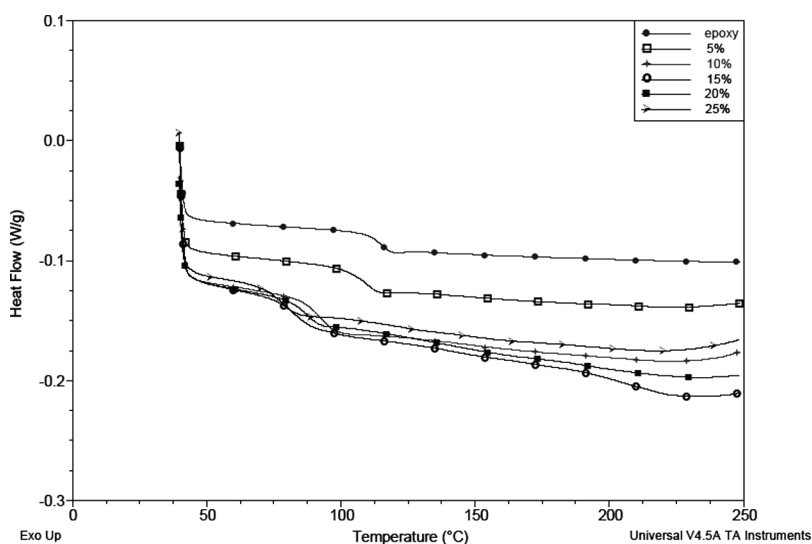


Figure 2: Variation of glass transition temperature with increase in PANI content.

that they cure at a very low temperature compared to Sn/Pb solder reflow temperature. This makes them suitable for attaching heat-sensitive components and substrates. Also, they were cured rapidly, which can save the time and lower cost.

Thermogravimetric Analysis (TGA)

TGA thermograms of ICAs with different PANI concentrations are given in Figure 3. Neat epoxy shows a small weight loss before 350°C which may be due to loss of volatiles and then undergoes a complete degradation around 600°C. TGA thermograms show that as the PANI is incorporated there appears a weight loss around 150°C which increases as the concentration of PANI increases. This may be attributed to loss of moisture and oligomers and is characteristic of the PANI phase. All the samples showed stability till 350°C and there is a steep weight loss till 450°C which is the feature of the epoxy system. Hence, it may be concluded that there is no significant effect of PANI on thermal degradation characteristics of the epoxy system.

Electrical Conductivity

Variation of electrical conductivity with the increase in PANI concentrations in ICAs is shown in Figure 4. The conductivity of the ICAs increases with the increase in PANI concentration from their typical insulating value of 10^{-14} to $\sim 10^{-3}$ S/cm for 25% PANI concentration. This occurs due to the formation of conducting channels by the distribution of PANI particles inside the epoxy

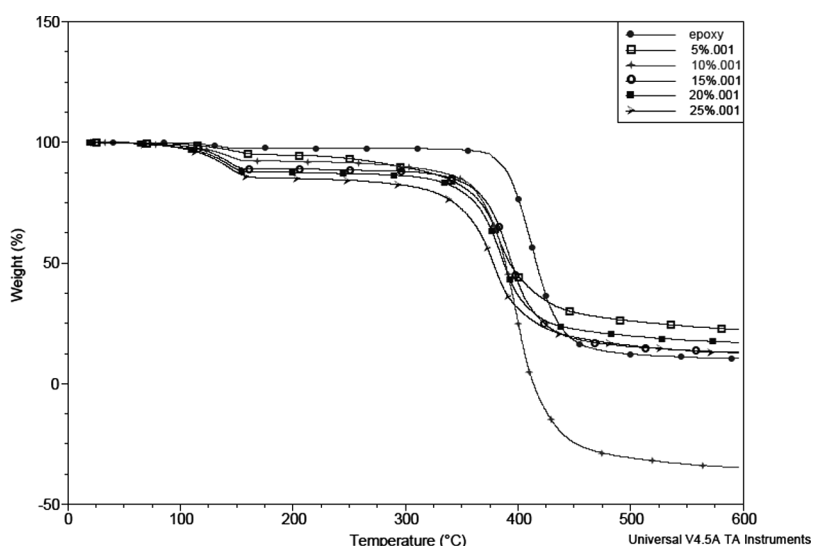


Figure 3: TGA thermograms of epoxy resin and epoxy/PANI composites.

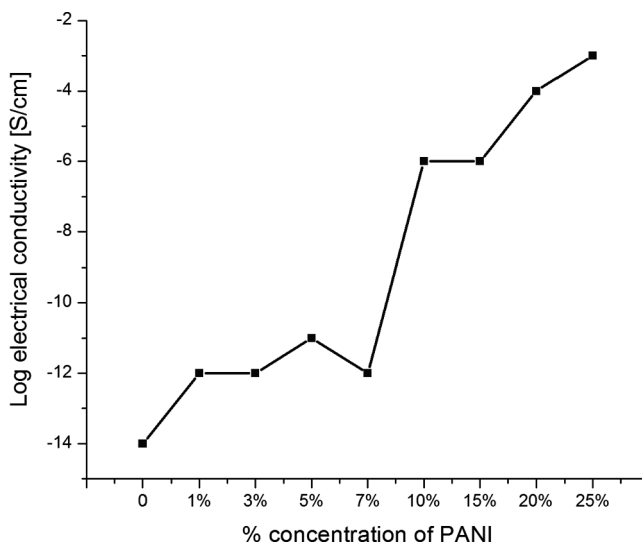


Figure 4: Electrical conductivity as a function of PANI concentration.

matrix. The percolation threshold (taken at 10^{-6}), i.e., the minimum amount of PANI which has to be added so that an infinite cluster of particles is formed throughout the sample which produces conductivity, is achieved by adding about 10% of PANI. For smaller concentrations of PANI, the conductivity remains low, but even 1% PANI increases the conductivity of the insulating matrix appreciably. This can occur due to encapsulation of the dispersed PANI from the epoxy matrix or by the formation of noncontinuous conductive paths because of low filler concentration [6].

Moisture Absorption

ICAs may be exposed to various environmental conditions during their service life. Moisture is commonly present in the service environment, and is one of the critical factors for determining the long-term reliability of adhesive bonded joints. Polymer systems are susceptible to warm, moist environments and can considerably alter the performance of the adhesives. Moisture absorbed in a polymer matrix can lead to a wide range of effects, both reversible and irreversible, including plasticization by weakening the intermolecular interactions among the functional groups of the chains. The degradation may be strongly affected by the presence and nature of fillers within adhesives, because the filler resin interface can be preferentially attacked by a particular environmental agent.

ICA samples were subjected to highly humid conditions and the observations with respect to weight change are given in Figure 5. It can be observed

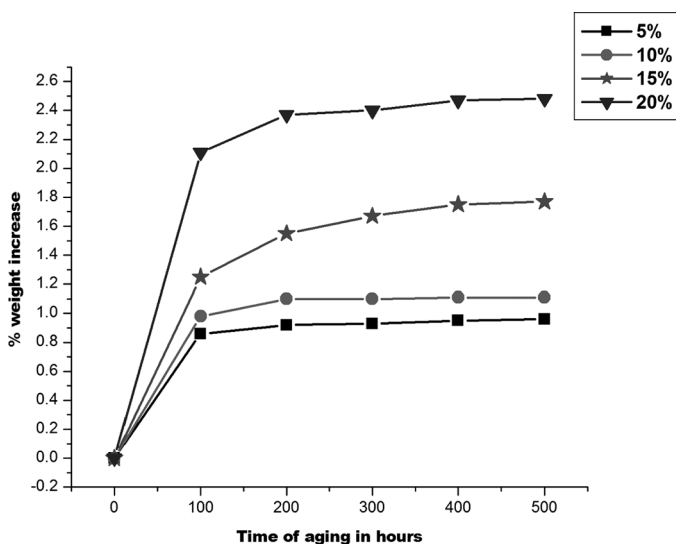


Figure 5: Moisture absorption behavior with increasing PANI content.

from the figure that all the samples exhibit rapid moisture uptake during first 100 h. This rapid gain may be due to the binding of water by the filler particles which are not strongly adhered to matrix network. These results are further complimented by the fact that weight gain increases with the increase in filler concentration as the proportion of the uncured part increases. Similar results for HHPA cured materials are reported earlier [14].

Drop Test

As per NCMS guidelines, an adhesive on a test assembly must pass 6 drops from a height of 60". The samples were studied for drop performance by recording the number of drops required to detach the chip from drop assembly. An average of five samples was taken for each adhesive sample and results are shown in Figure 6. All the samples except 25% PANI containing ICA showed no signs of fracture after 6 drops even if observed under a simple microscope. The ICA with 25% PANI showed fractures at the ends after the 5th drop and detached completely after 8 drops. The surface of the joint appeared very rough after curing for this adhesive. This may be due to the smaller proportion of curable epoxy system in this adhesive which imparts the impact strength. Samples were studied for drop performance after environmental aging at 85°C/~100%RH until 500 h. The results indicate that there was no significant effect on the drop performance of the samples after aging. Thus, these adhesives show impact stability under adverse environmental conditions.

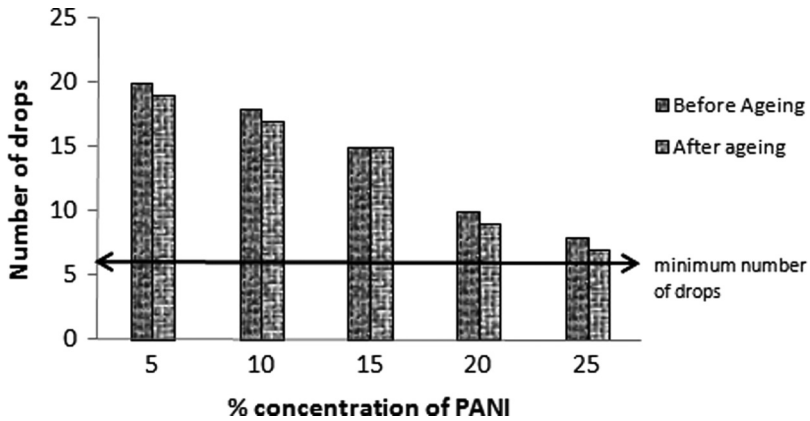


Figure 6: Drop test performance of ICAs.

Lap Shear Strength

Lap shear strength is another critical parameter for impact performance of ICAs. Five specimens of each ICA were studied and the average of these is reported. As shown in Figure 7, lap shear of adhesives decreases with increase in PANI concentration. This is due to hindrance caused by filler particles in adhesion of matrix network and decrease in the transmission of mechanical energy from the polymer matrix to the filler. But the bond between the matrix and filler particles is strong enough to impart the desired impact strength to ICAs. Test coupons with ICA having PANI concentration 25% broke while being fitted in the grips of UTM even before they could be pulled apart. Hence, the results of the same were not reported. It seems that at such a high concentration of PANI, filler particles disallow the effective formation of

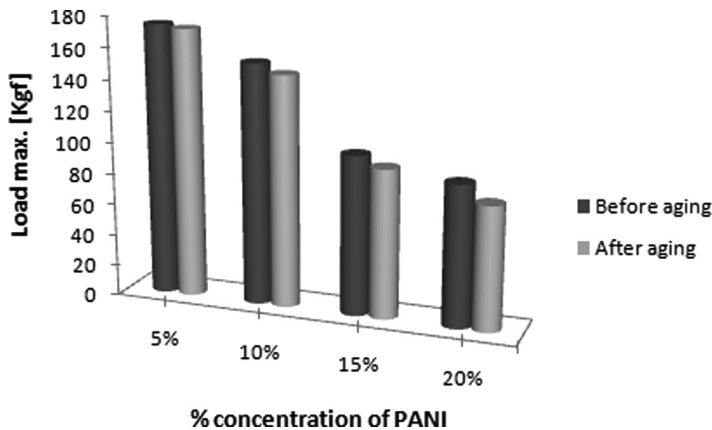


Figure 7: Lap shear strength of ICAs with different concentrations of PANI.

a matrix network. After aging at 85°C/ ~ 100%RH until 500 h, samples show a small decrease in lap shear strength, thus depicting that these adhesives do not show a significant damping of adhesive strength under harsh environmental conditions.

Scanning Electron Microscopy

The surface morphology of ICAs along with the neat epoxy was studied using scanning electron microscopy. Figure 8(a) shows a SEM micrograph of the neat epoxy matrix while Figure 8(b) that of as synthesized PANI and Figure 8(c) fractured surface of conductive adhesive prepared by epoxy with PANI in 5:1 ratio. It can be observed that PANI particles are dispersed within the epoxy matrix, yielding a conducting composite. There is no proper phase boundary between PANI particles and the epoxy matrix. This implies that the PANI particles are well-distributed within the matrix and there is a strong

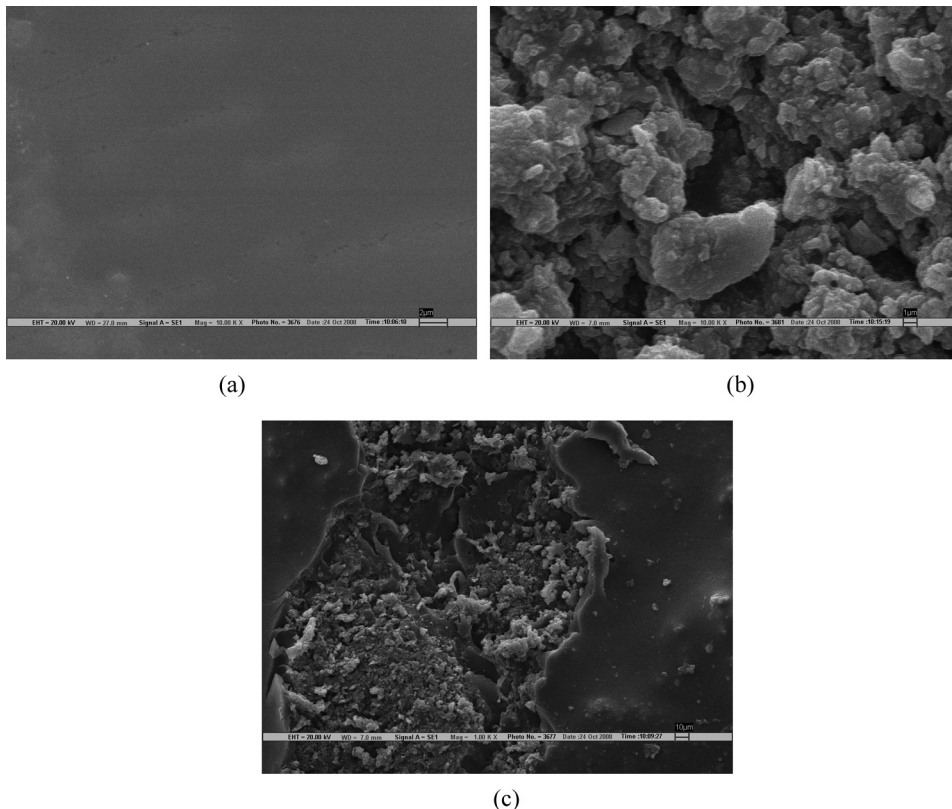


Figure 8: (a) SEM micrograph of neat epoxy matrix; (b) SEM micrograph of PANI; (c) SEM micrograph of composite with 20% PANI.

interaction between the matrix and the filler, which explains the cause of the good impact properties.

CONCLUSION

Composite samples with different concentrations of PANI in an epoxy/anhydride matrix were studied for their prospective use as an isotropically conductive adhesive. Thermal properties of the cured ICAs were studied using DSC and TGA techniques. It was observed from thermal studies that on adding PANI to resin, the T_g of the samples decreases which indicates that the presence of PANI affected the crosslinking of the epoxy matrix. The TGA thermograms were very close to that of a neat epoxy system. The impact properties, although affected by the PANI concentration, were substantially good as compared to ICAs with metal fillers. These improved impact properties are a direct consequence of using organic conducting polymer fillers instead of metallic filler due to a reduction in phase barrier. Electrical conductivity showed an increasing trend with the increase of PANI concentration. Although a conductivity of 10^{-3} S/cm was obtained at 25% PANI filler concentration, this ICA shows poor impact properties. From the interpretation of the results presented in this paper, we can conclude here that it is possible to produce isotropically conducting adhesives with improved impact properties by blending PANI in an epoxy matrix. Low conductivity can be a constraint which needs to be improved. Since blends were prepared by manual mixing of PANI powder with epoxy resin, there is a possibility of uneven distribution of filler particles to some extent. In order to get better impact properties and conductivity, PANI particles need to be finely dispersed in the matrix.

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