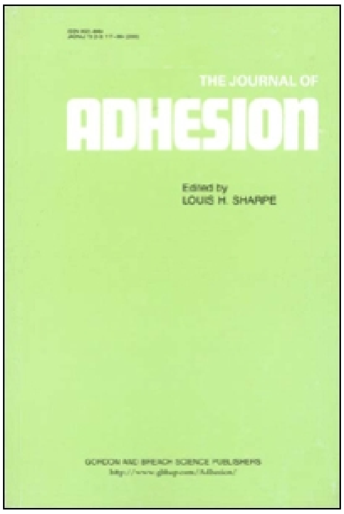

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Development of Polypyrrole/Epoxy Composites as Isotropically Conductive Adhesives

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Development of Polypyrrole/Epoxy Composites as Isotropically Conductive Adhesives

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As a possible replacement for lead bearing solders, metal filled isotropically conductive adhesives (ICAs) have shown a lot of potential recently. But still they have to come a long way and overcome their limitations like low impact strength and moisture instability. The current paper attempts to address the limitations of these ICAs by using intrinsically conducting polymer as a filler in place of metals. Conducting polymer (CP) polypyrrole (PPy) was incorporated as a filler in an epoxy/anhydride (EP) system and its application as an isotropic conductive adhesive was studied. PPy was synthesized by chemical polymerization using dodecyl-benzene sulphonic acid (DBSA) as dopant. The composites with varying PPy concentrations were studied for curing behavior and thermal degradation properties using DSC and TGA, respectively. The composites show good impact properties and conductivity at very low filler concentrations. SEM observations established that PPy particles were dispersed in the epoxy matrix uniformly. The overall characteristics of these conductive adhesives establish that they can be used as conductive adhesives in the electronics industry.

Keywords: Conducting polymers; Epoxy/Polypyrrole composites; Isotropically conductive adhesives; Solder replacement

1. INTRODUCTION

ICAs are perceived as next generation interconnect materials for electronic packaging because they provide an environmental friendly solution for interconnections in electronic applications, and they offer several potential advantages over conventional soldering

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technology, such as finer pitch printing, lower temperature processing, and more flexible and simpler processing. However, compared with mature soldering technology, conductive adhesive technology is relatively still in its infancy and some limitations and drawbacks do exist. The main limitations of current ICAs such as limited impact resistance, unstable contact resistance, and poor mechanical strength in various climatic and environmental conditions are major obstacles preventing ICAs from becoming a general replacement for solders in electronic applications [1].

In an attempt to address these limitations, we have developed ICAs with an intrinsically conducting polymer as a filler. Essentially, ICAs are fabricated using an adhesive matrix and a metallic conductive filler. Silver is most widely used as a conductive filler. It has been observed that metallic filler particles are responsible for the limitations of ICAs. Their presence inside the matrix decreases the impact strength and when exposed to moisture, they undergo corrosion and, hence, the contacts established are affected. Replacing metal fillers with CP has certain practical advantages. Since a polymer is introduced in the matrix network, the compatibility of the two phases increases and, thus, there is no need to add coupling agents as used in some metal-filled ICAs [2]. Also, at the contact interphase the possibility of corrosion is negligible. Hence, replacing metals by CP is a good approach to improve ICA properties and it is cost effective as well.

Among intrinsically conducting polymers, polypyrrole has shown wide range of applications due to its ease of synthesis, stability, and low cost. Some of its important properties include electrical conductivity, electroactivity, electrochromism, environmental stability, chemical stability, and corrosion inhibitive property. Because of these important properties, it is widely used in rechargeable batteries, electrochromic displays, ion-exchangers, pH sensors, gas sensors, and primers for corrosion protection of steel and aluminium. Difficulty in processing this polymer is a hindrance which prevents its effective use in many other applications. One of the most widely used techniques for improving its processing properties is by forming composites with other processable polymers. Blending PPy with epoxy has many advantages, such as smoother percolation curves and low process density as compared with metal fillers. In fact, specific masses of the epoxy matrix and the PPy particles are 1.23 and 1.4, respectively [3]. Although the approach seems to be viable, there are very few reports of such composites being available. Cassignol *et al.* reported the use of four methods to disperse increasing amounts of PPy in an epoxy matrix in order to make it electrically conductive. These composites were used to study the microstructure-conductivity relationship [4]. A correlation between percolation threshold and glass transition temperature depression in PPy/epoxy resin composites was observed by Barrau *et al.* [5]. Similarly, Pomposo *et al.* reported development of PPy-based conductive hot melt adhesives for EMI shielding applications [6].

In this paper, we report the possible application of PPy/epoxy composites as ICAs, a prospective alternative for replacing solders in electronic interconnections. PPy was synthesised by an *in-situ* chemical oxidation polymerisation using dodecyl-benzene sulphonic acid (DBSA) as dopant and $FeCl_3$ as oxidant. Varying the concentration of PPy in the epoxy matrix, different composites were prepared and studied for conductivity, impact properties, and thermal and morphological characteristics. ICAs with better stability and impact properties were developed.

2. EXPERIMENTAL

2.1. Materials

A bisphenol-F (DGEBF)-type epoxy resin, Epon 862, manufactured by Hexion speciality chemicals, Inc., Houston, TX, USA, was procured from Miller Stephenson Chemical Company, Inc., Danbury, CT, USA. It has an epoxy equivalent weight of approximately 170 g/equivalent. Anhydride hardener, hexahydropthalic anhydride (HHPA), and the catalyst, 2-ethyl-4-methylimidazole (2E4MZ), were obtained from Sigma Aldrich Chemicals Pvt. Ltd., Bangalore, India. Pyrrole was supplied by Sisco Research Laboratories Pvt. Ltd. Mumbai, India. DBSA was purchased from Himedia Laboratories Pvt. Ltd., Mumbai, India and $FeCl_3$ from Merck specialities Pvt. Ltd., Mumbai, India. Both were used as received.

2.2. Preparation of ICAs

2.2.1. Formulation of Resins

The resins for the ICAs were formulated according to the following procedure.

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

(b) The mixture was stirred 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.

2.2.2. Synthesis of PPy

Chemical polymerisation of pyrrole was done in a single step procedure [7]. 0.13 moles of freshly double distilled pyrrole and 0.13 moles of DBSA were dissolved in 100 mL of deionised Millipore® water by vigorous stirring to get a dispersion system. 0.26 moles of $FeCl_3$ were dissolved in 100 mL of deionised Millipore® water separately. The two solutions were cooled to ~0°C. Then the $FeCl_3$ solution was poured slowly over the dispersion of pyrrole and DBSA and kept at ~0°C. After 4 h excessive methanol was poured into the solution to terminate the reaction. The resulting polypyrrole precipitate was vacuum filtered and washed several times with distilled water, methanol, and acetone. Finally, it was dried in an oven at 80°C for 8–10 h, ground into fine powder, and stored in desiccators.

2.2.3. Preparation of Composites

Various amounts of PPy powder were added to the epoxy system to obtain composites with 5, 10, 15, and 20 weight percentage of PPy. The material was hand mixed thoroughly to obtain a uniform mixture.

3. CHARACTERIZATION

3.1. Cure Study

Curing profiles of the composite samples were studied by using a differential scanning calorimeter (DSC) from TA Instruments, New Castle, DE, USA, 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 hermetically sealed DSC pan and heated under a nitrogen purge. After the dynamic scan, samples were cooled to room temperature and scanned again at the same rate. Glass transition temperature (T_g) of the samples was derived from the mid-point of the curve of reversible heat flow *versus* temperature.

3.2. Thermogravimetric Analysis (TGA)

TGA thermograms of the composites were recorded using a TGA instrument, TA Instruments, New Castle, DE, USA, Model Q50, under nitrogen environment up to 600°C at a heating rate of 10°C/min.

3.3. Conductivity Measurement

Conductivity was measured by the four-probe technique on cured films of the ICAs. The procedure for laying films of the ICAs was as follows. 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 (Fig. 1). Using a square glass cover slip held at 45° angle, the adhesive was squeezed into the space. The cover slip rides on the tape and provides a uniform film of the adhesive of about 3-micron thickness. The tape was removed and the glass slides were placed in a 150°C pre-heated oven for 1 h. After cure, the samples were dipped in acetone for 2–3 h until solvent swelling occurred and peeled off the glass slide using a doctor blade. The films were dried in an oven at 60°C and kept for 1 day before the conductivity test. Conductivity was measured by means of the standard in-line, four-probe method using a semiconductor characterization system from Keithley Instruments, Inc., Cleveland, OH, USA, Model 4200. Both surfaces of the films were scratched using flint paper before measurements to ensure proper contact. An average of 12 measurements was taken for each sample.

3.4. Impact Performance

Drop tests were conducted based on the standard established by National Center of Manufacturing Sciences (NCMS), USA, as per the procedure reported earlier [8]. In this test, a mounted chip carrier and circuit board assembly are dropped onto hard surfaces 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.

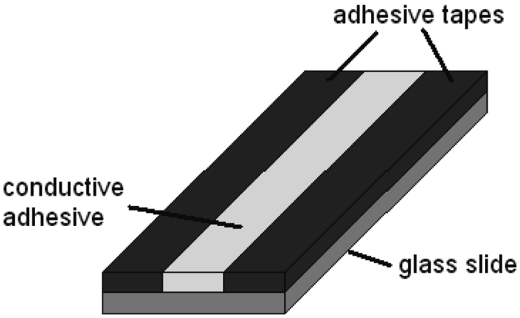


FIGURE 1 Composite sample on a glass slide.

3.5. Moisture Absorption Measurement

Moisture absorption tests were performed on bulk samples by conditioning at 85°C/~100% RH for 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 Mettler Instruments, Greifensee, Switzerland, 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 ageing 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 [9].

3.6. Lap-Shear Strength Test

A lap-shear test determines the lap-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 according to ASTM D3163 specifications. Two specimens with polyimide material on one side and copper surface on the other and of dimensions 1×4 inch (2.5×10 cm) are bonded together with the adhesive so that the overlap area is 1×1 inch (2.5×2.5 cm). The overlap area was abraded by 150 grit flint paper prior to bonding with the adhesive to be tested. The adhesive was applied between the abraded panels and clamped in place. The thickness was maintained using end strands of a lead wire of diameter 0.1 mm. After curing, the cooled specimens were pulled apart by an Electronic Universal Testing Machine (UTM), Model 3369, from Instron, High Wycombe, UK at a pull rate of 0.05 in/min (0.13 cm/min) and the peak stress was determined. Two groups of specimens were prepared. In each group, five samples were prepared for every kind of ICA. One group was tested after cure, and the second was tested after conditioning for 200 h at 85°C/~100% RH.

3.7. Scanning Electron Microscopy

Scanning electron micrographs (SEM) were obtained with a ZEISS EVO series scanning electron microscope, Model EVO50, from Carl Zeiss SMT Ltd., Cambridge, UK, 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.

4. RESULTS AND DISCUSSION

4.1. Conductivity Measurements

The conductivity of the composites with different concentrations of PPy was measured. In order to obtain consistent results, identical conditions were maintained. Figure 2 shows the evolution of conductivity in the composites as the concentration of PPy increases. With respect to the parent epoxy network, the conductivity shows a sharp increase even with the incorporation of only 3% of PPy. Even the threshold percolation taken at 10^{-6} S/cm (S = siemens) comes at a lower PPy concentration, *i.e.*, between 5–10%. PPy formed by dispersion polymerisation has a very minute and uniform particle size and is, thus, easily dispersed in the epoxy matrix to form a conductive network. At the percolation threshold this network becomes continuous and an infinite cluster of PPy particles is formed which ensures conduction within the insulating matrix network. These results are in accordance with those reported by Cassignol *et al.* [4] and Barrau *et al.* [5]. With the increase in PPy concentration, conductivity shows a smooth increase till it reaches a value of 10^{-3} S/cm with a PPy concentration of 15%. Above this concentration there was no significant increase in

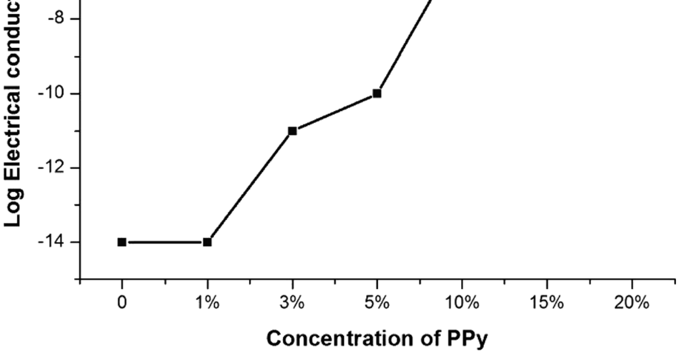


FIGURE 2 Variation of electrical conductivity with increase in PPy concentration.

conductivity, which may be due to saturation in conductive filler distribution and formation of clusters.

4.2. Curing Properties

The DSC thermograms of uncured epoxy/PPy composites along with that of the neat epoxy/anhydride system are presented in Fig. 3. It can be observed that a single exothermic peak is evident in all samples irrespective of the concentration of PPy in the epoxy matrix. Hence, it is clear that the basic curing profile of the epoxy anhydride system is not changed by the incorporation of PPy. The epoxy anhydride system shows a sharp exothermic peak at about 138°C corresponding to complete cross linking of the matrix. However, with the increase in PPy content the peak starts to broaden and is slightly shifted towards higher temperature. This may be due to decrease in the curable epoxy concentration in the composites and, thus, increase in the curing time. ICA with 10% PPy concentration shows a slight shift towards low temperature. It may be worthwhile to note that the percolation threshold of the composites is around this concentration. Below the percolation threshold the filler particles form random clusters but around the threshold percolation the particles form a definite pattern and, thus, an arranged pattern of filler particles is formed. This, in turn, has a definite effect on network formation

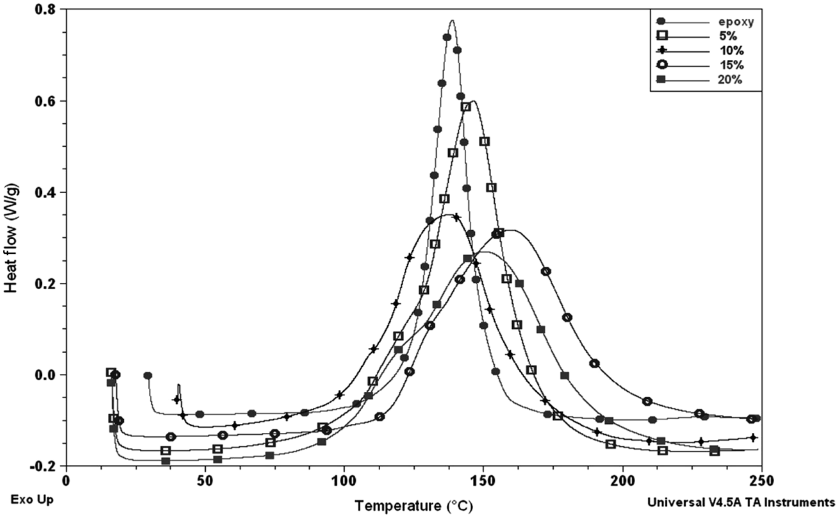


FIGURE 3 DSC thermograms of PPy/epoxy composites.

during curing and there is minimal hindrance due to PPy particles. This trend is further confirmed by the sharp depression in glass transition temperature (T_g) of this composite.

After the DSC scan, samples were cooled to room temperature and scanned again at the same rate to obtain glass transition temperature (T_g) of the samples. Variation of glass transition temperature with the increase of PPy concentrations is shown in Fig. 4. At a low PPy concentration of 5%, T_g increases but it decreases when the PPy concentration becomes 10%. This unusual behaviour was confirmed with a number of repeated scans and it seems to be independent of epoxy resin curing. As the concentration is around the percolation threshold of the composites, there is a depression of T_g. This depression in T_g has been reported by Barrau *et al.* [5]. It has been concluded that the increase of T_g with increase in PPy concentration is a direct consequence of the higher T_g of PPy as expected for compatible polymer blends. The depression in T_g around the percolation threshold is interpreted as an increase in the mobility of epoxy matrix chain segments. The transition at the percolation threshold is related to formation of infinite clusters due to which free volume accessible to molecular motion of epoxy chain segments is maximal [5].

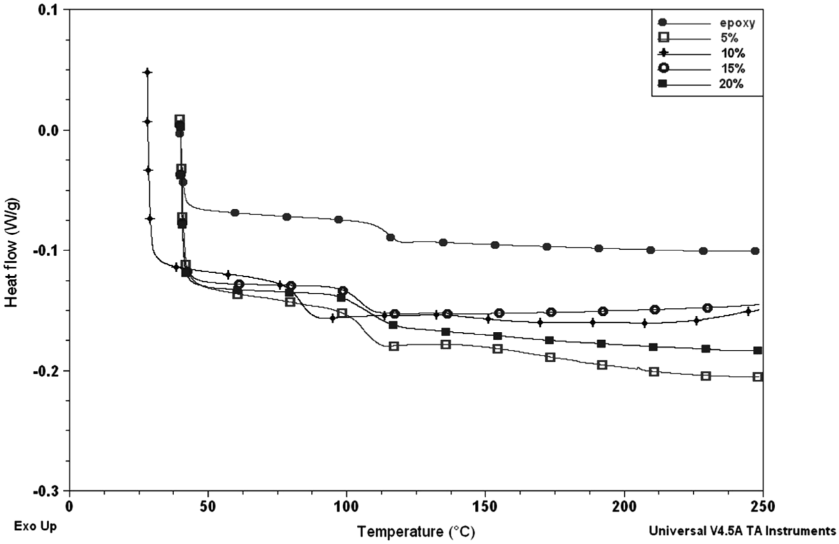


FIGURE 4 Variation of glass transition temperature with increase in PPy concentration.

4.3. Thermogravimetric Analysis

Thermal stability of the samples was studied by TGA analysis and is depicted in Fig. 5. All the samples essentially show a two-step transition. The epoxy system shows a slight weight loss around 150°C which can be due to loss of volatiles and is stable until around 400°C, after which it shows a steep degradation. With incorporation of PPy the basic degradation characteristics are essentially same, with a sequence of two-step degradation. But with the increase in PPy content, the weight loss around 150°C increases. This is probably due to loss of volatiles and oligomers and is characteristic of the PPy phase. All the samples showed stability untill 350°C and then underwent a sharp degradation at 450°C which is essentially the characteristic of the epoxy system. Hence, it can be observed from the results obtained that PPy incorporation does not have a significant effect on the thermal degradation of the epoxy systems.

4.4. Moisture Absorption

Resistance to moisture is a very important parameter of ICAs. Moisture present in the service environment can degrade the impact properties of the adhesives, by giving rise to swelling stresses in the system. This may lead to formation of voids or growth of already present voids. Water may also affect the electrical properties of the

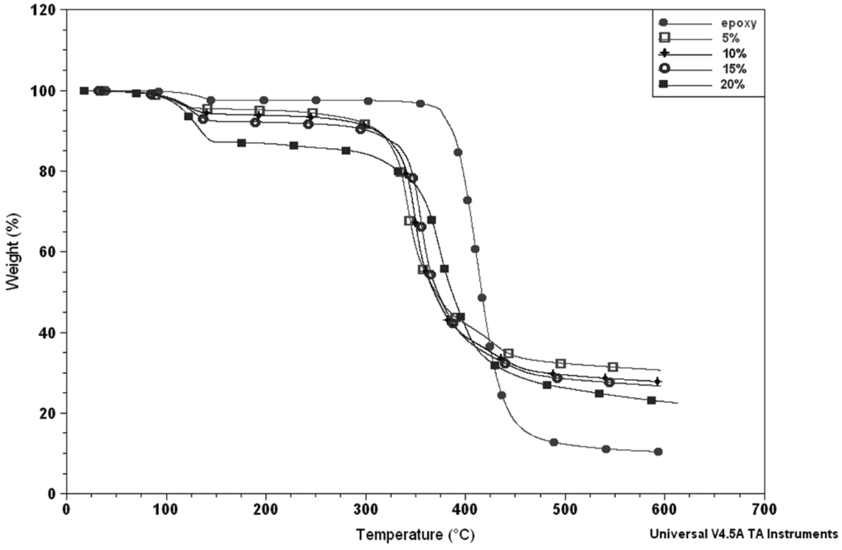


FIGURE 5 TGA thermograms of PPy/epoxy composites.

adhesives and form oxides on the surface of metal fixtures attached by them. Hence, good ICAs should have very low moisture pickup capacity. Moisture absorption data obtained after 85°C/~100% RH ageing is presented as percent weight gain in Fig. 6. It can be observed that even cured ICAs show moisture absorption but the weight gain is small. Moisture uptake of samples was more during the first 100 h. This may be due to water attached to the filler particles which are not completely adhered to the epoxy matrix network. PPy has a known affinity towards humidity [3]. This is attributed to the presence of heteroatoms and disordered structure of PPy which favours penetration of small atoms like water. These molecules are free or may be linked by hydrogen bonds to NH groups [3]. In all the samples there is almost saturation beyond 100 h. These results are further complemented by the fact that as the percentage of PPy increases, the weight gain increases, which indicates that the moisture uptake is a due to increase in concentration of PPy with respect to the cured epoxy matrix. However, the results are indicative of the fact that even under harsh conditions of temperature and humidity, ICAs showed phenomenal stability and the weight gain was small even after 500 h of exposure.

4.5. Drop Test Performance

High impact strength is a very important property of high performance conductive adhesives. ICA joints have to absorb shocks during

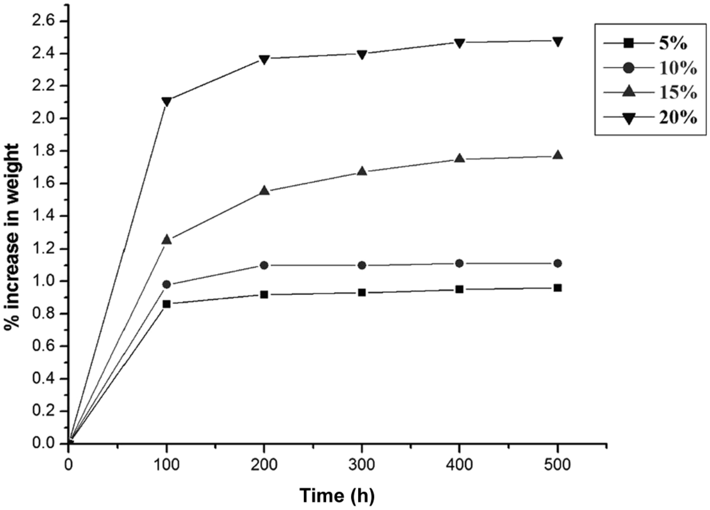


FIGURE 6 Moisture uptake of composites.

assembling, handling, and throughout their service life and, thus, need to exhibit extremely good impact properties. Impact performance of any material depends on the effective damping property, *i.e.*, the capacity of a material to dissipate energy. The impact performance of ICAs was determined using a drop test devised by NCMS, USA. For an ICA to be used for solder replacement, it has to survive six drops from a height of 60 inches without the test assembly being detached. In this study, drop tests were performed by dropping the test assembly through a channel on to a concrete floor, ensuring that it falls vertically. An average of five tests was done and the results are shown in Fig. 7. Since the powder of PPy formed is smooth and the particle size is small, the impact performance of the epoxy is not affected significantly. It can be observed that assemblies bound by ICAs containing 5 and 10% PPy were stable even after 25 drops and the trend was not changed by ageing the samples in 80°C/~100% RH for 500 h. All the sample assemblies after ageing continued to be intact long after the required minimum of six drops. But with the increase in PPy concentration, drop performance decreased slightly. This again leads to the fact that moisture absorbed by partially free PPy particles leads to void propagation and, thus, decreases the impact performance. Although drop performance decreases with increase in PPy

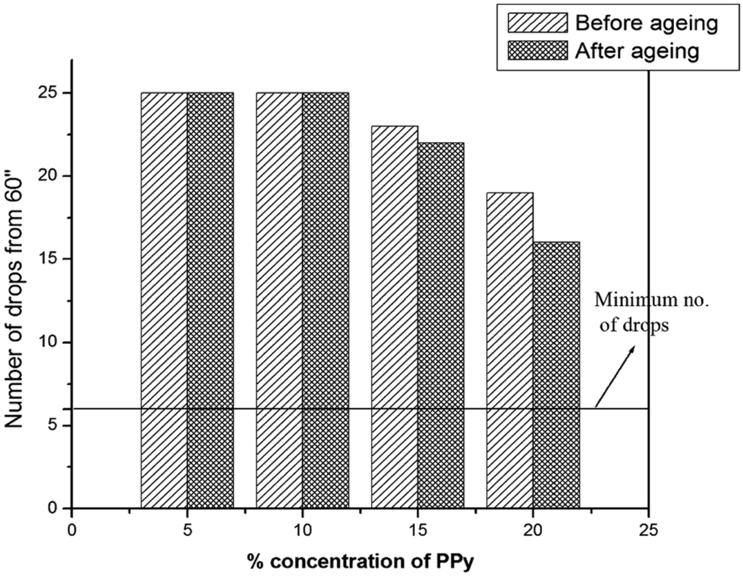


FIGURE 7 Drop test performance of ICAs.

concentration these ICAs are far more stable and can withstand the shocks even after exposure to a very harsh service environment.

4.6. Lap-Shear Strength

Representative data on lap-shear results are shown in Fig. 8. In all the cases there was a drop in lap-shear strength with the incorporation of PPy in the epoxy matrix. However, it is significant to note that after a sharp decrease in lap-shear at 5% PPy concentration, there is only a slight change in lap-shear thereafter. It is indicative of the fact that since the particle size of PPy is uniform and small, there is an even dispersion of particles within the epoxy network without formation of agglomerates. In most of the composites there was almost no effect of ageing on lap-shear properties. When the PPy concentration increased beyond 15%, the lap-shear decreased. There is probably a hint of PPy phase domination beyond that concentration and, hence, moisture might be enhancing the crack or void propagation leading to decrease in lap-shear. Overall, it can be observed that these composites do not show a damping of adhesive strength under adverse environmental conditions.

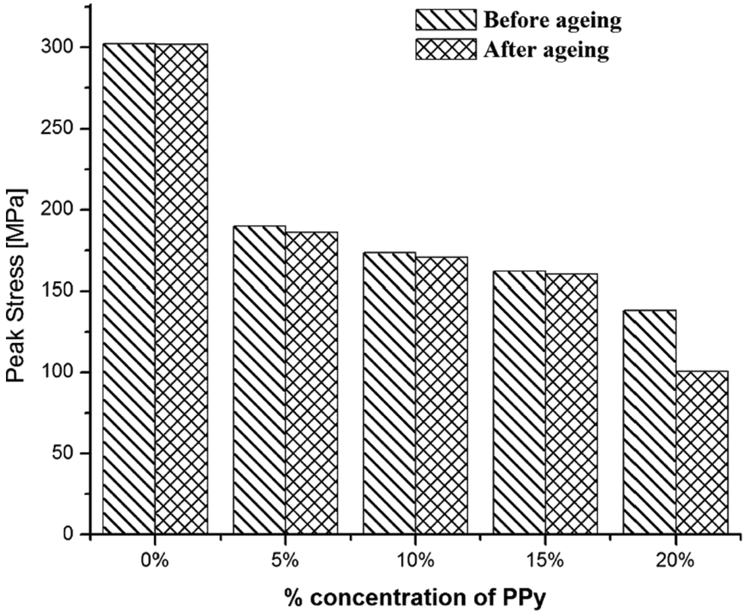
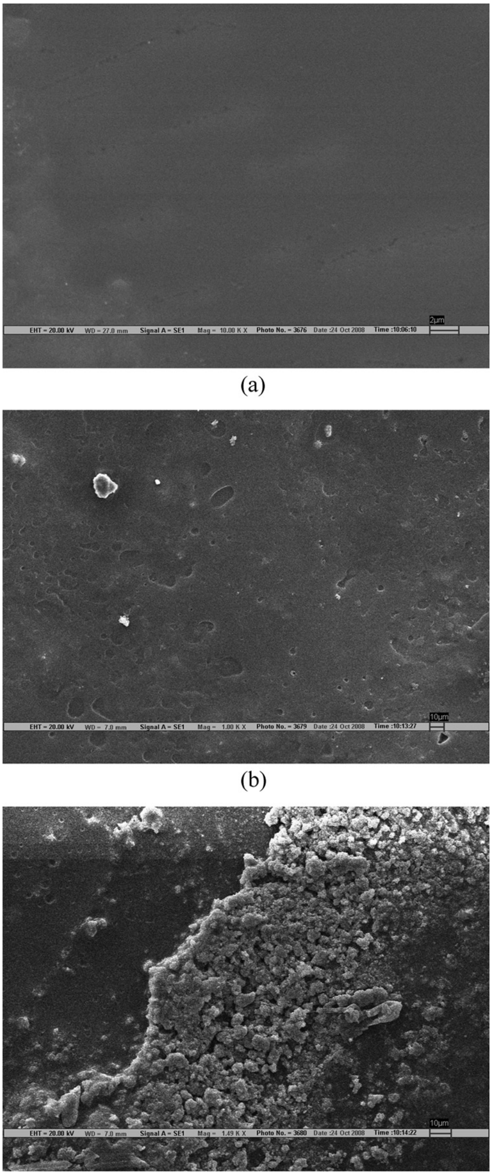


FIGURE 8 Lap-shear strength of the ICAs.

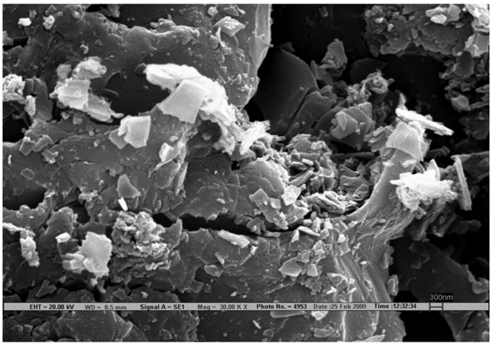


(a)

(b)

(c)

FIGURE 9 (a) SEM micrograph of neat epoxy matrix. The scale marker is 2 μm. (b) SEM micrograph of epoxy/PPy composite surface. The scale marker is 10 μm. (c) SEM micrograph of epoxy/PPy composites. The scale marker is 10 μm. (d) SEM micrograph of epoxy/PPy composite at very high magnification. The scale marker is 300 nm.



(d)

FIGURE 9 Continued.

4.7. Scanning Electron Microscopy

The microstructure of PPy incorporation was observed by scanning electron microscopy. Figure 9(a) shows the surface of neat epoxy-cured film which depicts a smooth textured contourless structure. Figure 9(b) shows the surface of the epoxy/PPy composite without any distinct agglomeration of PPy particles. Some particles appear on the surface while few appear partially embedded inside the matrix. It may be observed that the smooth textured surface of epoxy matrix has developed contours due to PPy particles. The distribution of these PPy particles in the hard epoxy matrix is a bit difficult to see in the SEM. An image of a peel fractured ICA film, Fig. 9(c), shows a cluster of PPy particles which have a strong interconnection with the epoxy matrix and the particles seem to be well connected without a definite phase separation. When the fractured surface of these samples was observed under very high magnification, PPy particles were very difficult to identify and appeared to be deeply embedded inside the crosslinked epoxy matrix, Fig. 9(d). All these observations clearly establish that PPy particles are easily distributed within epoxy matrix and do not lose their identity while forming close connecting patterns which act as paths for conductivity.

5. CONCLUSION

Composites of PPy with an epoxy anhydride system show prospects of being used as ICAs, although conductivity needs further improvement. PPy particles are easily dispersed within the epoxy matrix without affecting its basic properties. Conductivity shows a smooth increasing trend and reaches a value of 10^{-3} S/cm with a PPy concentration as low as 15 wt.%. No further increase of conductivity was observed on increasing the concentration of PPy. The thermal properties and curing profile of the composites are very close to that of the neat epoxy system. However, a depression in T_g was observed close to threshold percolation due to increased mobility of polymeric chains around that concentration. Impact properties of the epoxy matrix are affected but are still good enough for an ICA. Moisture shows a negligible effect on the overall properties of the ICAs studied. Hence, incorporation of PPy in the epoxy matrix forms composites which may be used as ICAs in electronic interconnections. The composite with 15 wt.% PPy showed the best properties and can be most suited for the application.

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REFERENCES

[1] Mir, I. A. and Kumar, D., *Int. J. Adhes. Adhes.* **28**, 362–371 (2008).

[2] Tan, F., Qiao, X., Chen, J., and Wang, H., *Int. J. Adhes. Adhes.* **26**, 406–413 (2006).

[3] Cassignol, C., Olivier, P., and Ricard, A., *J. Appl. Polym. Sci.* **70**, 1567–1577 (1998).

[4] Cassignol, C., Caveraro, M., Boudet, A., and Ricard, A., *Polymer.* **40**, 1139–1151 (1999).

[5] Barrau, S., Demont, P., Meraval, C., Bernes, A., and Lacabanne, C., *Macromol. Rapid Commun.* **26**, 390–394 (2005).

[6] Pomposo, J. A., Rodriguez, J., and Grande, H., *Synth. Met.* **104**, 107–111 (1999).

[7] He, C., Yang, C., and Li, Y., *Synth. Met.* **139**, 539–545 (2003).

[8] Rao, Y., Lu, Daoqiang, and Wong, C. P., *Int. J. Adhes. Adhes.* **24**, 449–453 (2004).

[9] Xu, S., Dillard, D. A., and Dillard, J. G., *Int. J. Adhes. Adhes.* **23**, 235–250 (2003).