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Characterization of metal-polymer interaction forces by AFM for insert molding applications

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Abstract
There is a growing interest in the overmolding of electronics with thermoplastics and the embedding of electronics in 3D printed parts. However long term device reliability requires good adhesion between the metallic surfaces of the electronic components and the overmolding polymer. In order to provide a guide to material selection, interaction forces between tin, a common electronics metallization and six commodity thermoplastics were studied. The force measurements were undertaken using atomic force microscopy (AFM) with probes functionalized with tin particles. The particles were attached to the probes by a novel method using a focused ion beam (FIB) instrument. Highly consistent cantilever deflections at pull-off were obtained, allowing the thermoplastics to be robustly ranked by strength of interaction with tin as: PC > PMMA > PBT > ABS > PS > PA 6. From consideration of possible contributions to the pull-off forces measured, it was concluded the data and the developed AFM tip functionalization technique are likely to be useful in materials selection for electronics overmolding with thermoplastics. The FIB functionalization technique may be useful in the wider context of investigations of other metal-polymer interaction forces, for example with alloys, where other methods of functionalization may be difficult to apply.

KEYWORDS
adhesion, atomic force microscopy, atomic interactions, electronics, force-distance mode, functionalization, insert-molding, metal-polymer

1 | INTRODUCTION

The most common printed circuit board (PCB) substrate material, FR4, consists of an epoxy based resin with woven glass fiber reinforcement[1] and has been successfully used for many decades. However, the inherent lack of recyclability of the composite has created end-of-life disposal problems. Environmental legislation related to electronic and electrical equipment, such as the European Union directives on waste[2] and on hazardous substances[3] has led to manufacturers looking for more environmentally friendly options to manufacture electronics. Thermoplastics are readily recyclable and hence are being investigated as direct one-to-one replacements for thermoset-glass fiber PCBs.[4] Thermoplastics are already the base material for molded interconnect devices (MIDs) which are used for 3D interconnection in several applications including automotive.[5-7]

Polymer overmolding or embedding of electronics has also been proposed as a viable "greener" alternative to conventional PCB technology.[8,9] In many cases, the aim is to remove the need for a substrate altogether and encapsulate the components and interconnecting tracks within the surrounding polymer matrix. The "Occam" process[10] is an example of this and uses thermoset resins as the matrix to produce circuits in a build-up manner similar to embedded chip packaging techniques. However, as the process uses thermoset resins the environmental benefit envisaged is reduction of energy use by avoiding a soldering step, rather than an improved end of life disposal profile. In order to use recyclable thermoplastics instead, in conjunction with higher volume injection molding methods, an alternative process, termed "Substrateless Packaging", has been demonstrated, that involves insert molding, with the electronic components as the inserts, and a thermoplastic as the overmold.[11] The molding procedure leaves the interconnection features of the components (legs or pads) exposed and interconnect is achieved by then printing or plating a conductive material onto the molding. As an extension of these approaches, there has also been much recent interest in 3D printing of polymeric devices with embedded electronics.[12-14] In many cases, these also utilize thermoplastics that can be deposited by fused deposition modeling (FDM) to build the encapsulating structure within which the electronics is embedded. There has therefore been much progress in the replacement of thermosets with thermoplastics in the fabrication of electronic devices, for which methods that enable the easy separation of organic and inorganic matter for end-of-life processes and recycling are also being investigated.

In substrateless packaging and other overmolding/embedding technologies, intimate contact between the thermoplastic resin, and the metallization of the electronic components, is crucial for the integrity of the electrical interconnection, as illustrated in Figure 1. If small gaps open up around the embedded components in the surface of the polymer after solidification these will either act as failure points or prevent interconnection altogether with the circuit pattern that is formed on the surface. Similarly, any gaps in other locations may present areas where moisture can accumulate over time, leading to corrosion and component failure, or relative movement during expansion / contraction may lead to fatigue failure. The question of what material-material interactions, and process conditions, promote adhesion between insert and overmold is therefore a crucial one to address to enable production of high quality and reliable substrateless/embedded circuits. However, there is little published in the scientific literature on the adhesion or interaction forces between insert and molding, and most of the information in the public domain is empirical in nature.[15]

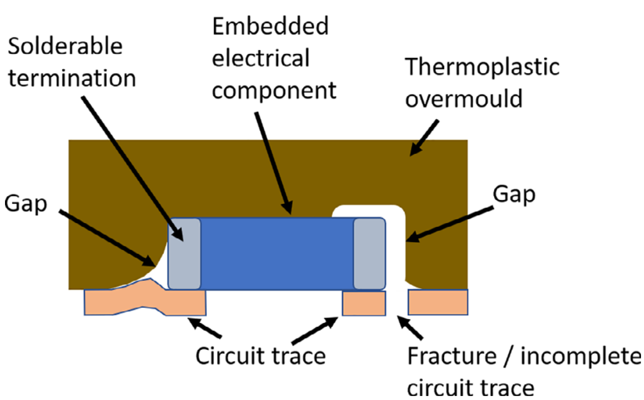

FIGURE 1 Schematic diagram illustrating where gaps may occur in substrateless/overmolded devices [Color figure can be viewed at wileyonlinelibrary.com]

The interactions that would be expected to have an effect on adhesion between electronic component metallization surfaces and a thermoplastic overmold are: (a) solid-solid insert-overmold interfacial adhesive forces; (b) the wetting interaction of the thermoplastic in the melt at high temperature with the component surfaces; and, (c) the residual stress state of the polymer, which would be strongly affected by the presence of the insert through its influence on the thermal history of the molding. Related work on melt wetting and residual stress have been published elsewhere.[16]

In the work reported here, the solid-solid interfacial forces between a typical component metallization and surrounding thermoplastic in the solidified overmold, together with a suitable technique to determine them were investigated, with the goal of being able to identify which materials give the strongest interactions. Such information can be used to inform process development for future manufacturing systems involving embedded electronic components. Tin was chosen as the metal of interest, in order to represent the surface metallization of a large proportion of electronic components. Its interaction was studied with six different thermoplastics that were chosen as likely candidates for commercial overmolding applications, combining good native fire retardancy properties with low cost and existing use in electronic products.

The technique chosen to study the solid-solid interfacial forces was atomic force microscopy (AFM) operating in the force-distance mode (Figure 2). In this mode a silicon probe cantilever with a pyramidal shaped probe tip - see Figure 3, is moved with nanometer precision towards or away from a surface, while simultaneously the deflection of the cantilever, δ_c under the influence of surface-

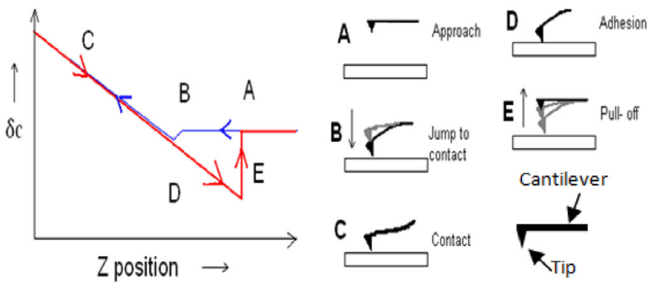

FIGURE 2 Ideal AFM force-distance curve with labeling corresponding to tip-sample interaction regimes - δ_c is cantilever deflection [Color figure can be viewed at wileyonlinelibrary.com]

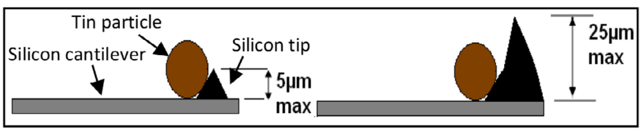

FIGURE 3 Diagram showing adhesive attachment and relative sizes of a 10 μm diameter tin particle compared to the tip on DNP-10 (left), and TESP (right), cantilevers [Color figure can be viewed at wileyonlinelibrary.com]

surface interactions is measured. Force can be inferred from knowledge of the spring constant of the cantilever. Many studies have used AFM to identify and quantify the interatomic interactions between materials. Capella and Dietler, Butt et al. and Ralston et al. have written comprehensive guides on force measurements with the atomic force microscope, explaining technique, interpretation and applications.[17-19] An ideal force distance plot is shown in Figure 2, together with the various positions of the cantilever. The blue line represents the extending plot, that is, measurements during the approach of the cantilever to the surface, and the red line represents the retracting plot. At stage A the cantilever is approaching the surface and δ_c is 0 (noncontact regime). At a critical distance, that is, at stage B, the cantilever jumps into contact with the surface due to the interactions between the tip and the surface (contact regime). It should be noted that the jump-to-contact feature is not always seen. In stage C the cantilever mounting continues towards the surface, causing the cantilever to bend. The mounting is then retracted, stage D, during which the cantilever tip remains in contact with the surface due to the adhesive forces. At a certain point, E, the elastic force due to the flexure of the cantilever is sufficient to overcome the adhesive forces between the tip and the sample, and the tip separates from the sample surface, known as pull-off. The size of the deflection at pull-off can be used to estimate the forces of adhesion between the probe and the substrate.

In order to determine interactions between a chosen pair of materials, one of the materials of interest must be attached or coated onto the cantilever tip to functionalize it. While tips can be functionalized with coatings, for example, gold, these can be limited by the deposition techniques available (eg, physical vapor deposition) so that mixed materials, such as alloys, may not be easily explored. Methods for functionalization by the attachment of a distinct particle to the tip have also been developed. Gan has written a detailed critique about the various particle attachment techniques to AFM probes for surface force measurements[20] and a support note supplied by AFM manufacturer Veeco also covers the methods to attach particles to AFM cantilevers.[21] Some of these techniques are: using an adhesive,[22] high temperature sintering of borosilicate glass,[23] attachment of nanoparticles[23-26] and direct deposition by use of a focused electron beam to "weld" the particle of interest to the AFM cantilever.[23] The advantages and disadvantages of these techniques have been discussed elsewhere in detail[20] but briefly, the use of high temperature sintering is limited to borosilicate glass particles while grafting and wet chemistry surface assembly techniques are suitable only if the particles are nanosize. Typically, gluing of particles and direct deposition techniques are used to functionalize the AFM tip when the particle size is in μm. Each of these techniques requires customized instrumentation and expertise and the selection of a technique depends upon the availability of resources and the nature of the functionalization needed. Using these particle attachment techniques, a number of adhesion studies have been reported. Wiling et al. obtained maps of the adhesion between an individual lactose particle attached to a tip and gelatin capsules.[27] Schaefer and Gomez also obtained maps of adhesion and have described "jump mode" as a way of mapping adhesion for a surface.[28] Eve et al. brought a salbutamol functionalized AFM tip to various surfaces of interest and used this to rank its adhesion with glass, PTFE and other materials.[22]

Use of an AFM to understand adhesion at the material level and linking it to the macroscopic level has also been attempted before. Schirmeisen et al. calculated the force of adhesion between aluminum and polycarbonate and tried to compare the theoretical work of adhesion results with stud pull out tests. They concluded that the adhesion strength suggested by the AFM force-distance measurement is much higher than that of the mechanical strength test.[29] Wong et al. used AFM to characterize the nanoscale adhesion force in a Cu-SAM-EMC system and used it as a criterion for selection of the SAM. The results were shown to be consistent with the results of macroscopic shear tests.[30] Han et al. used (AFM) pull-off measurements to predict adhesion at the solid-solid interface. The results were compared to microvalves that had been fabricated with different surfaces at the seat/membrane interface, and they found good correlation between the AFM results and the macroscopic measurements.[31] This type of measurement has also been used to characterize the adhesive properties of polymer microstructures.[32]

In support of the aims of this study a novel method of attaching a particle of tin to an AFM cantilever tip to functionalize it, using a focused ion beam (FIB) apparatus was developed and is reported here. Probes fabricated in this way were used to probe the material-material interaction forces between tin and granules of six commodity thermoplastics: polyamide 6 (PA 6), polycarbonate (PC), polymethyl methacrylate (PMMA), polystyrene (PS), acrylonitrile butadiene styrene (ABS) and polybutylene terephthalate (PBT). The results obtained with the tin/thermoplastic pairs are presented and the validity of the results and the implications for the integrity of substrateless/embedded circuits employing overmolding of electronic components are discussed. It is also proposed that the FIB probe functionalization technique may be of wider use beyond the present application in investigating polymer-metal interactions for metals other than tin, in particular alloys, where other methods of functionalization may not be practical.

2 | EXPERIMENTAL DETAILS

A Dimension 3100 AFM from Veeco (Digital Instruments) was used for this experiment and can be operated in both tapping and contact mode. Nanoscope 6.12rl was the software interface (also provided by Veeco) that was used to record the data. The AFM cantilever tips were TESP probes from Veeco with nominal properties as follows: Thickness-range: 3.25-4.75 μm; Length-range: 110-140 μm; Width-range: 30-50 μm; f_0 (frequency) range: 230-410 kHz; k (spring constant) range: 20-80 N/m; Material: 0.01-0.025 ohm-cm Antimony (n) doped Si; Coating: None.

Tin particles from Goodfellow (average size 45 μm 99.9% pure) were used to functionalize the AFM cantilevers. When observed under a scanning electron microscope, the size of the tin particles was found to vary from around 15 μm upwards. Not all of the particles were spherical. Based on other studies using particle functionalized AFM cantilevers, particles of size 15 +/− 2 μm were chosen for this work. The attachment of the tin particles to the AFM tips was achieved using an FEI Nova 600 Nanolab dual beam focused ion beam/scanning electron microscope (FIB/SEM). It consists of a gallium source focused ion beam column and high-resolution field emission gun electron beam column thereby enabling sample preparation and imaging within the same instrument.

The polymer samples used for these experiments were injection molding granules as received from the manufacturers. These were used to avoid risk of surface contamination from additional processing steps, for example, mold release agent, coming in contact with the sample surface. The granules were however dried before the experiments in a fan oven for the time and temperature recommended by the manufacturers for injection molding processing. The grades of the materials used were PC: Calibre 301-10 from Dow (Ashland), PS: Styron 634 from Rapra, ABS: Polylac PA-747 from Chi Mei Corporation, PBT: Celanex 2500 from Ticona, PMMA: Plexiglas 8 N (Glasklar) from Rohm, and PA 6: Ravamid R 200 S from Ravago.

3 | TIP FUNCTIONALISATION

Initial trials were performed with Veeco DNP-10 cantilevers functionalized by adhering the tin particles adjacent to the tip, as shown in Figure 3. However, it was found that the cantilever stiffness was too low to allow measurement of the pull-off forces developed. The stiffer TESP cantilever was then selected, but, as Figure 3 illustrates, due to the larger tip size and the location of the particle at the base of the tip, a prohibitively large tin particle would have been required to allow use of the adhesion functionalization method. A technique of particle attachment was therefore adapted from work done by Sqalli et al..[23] The new technique relies on a dual beam FIB/SEM system with a micromanipulator attachment to place the particle directly on the tip rather than at its base.[33]

To functionalize the AFM cantilevers a selection of tin particles were spread on a gold plated glass slide and placed in the vacuum chamber of the dual beam FIB/SEM and, after imaging, one with a size of 15 +/− 2 μm was selected for use. The tip of the FIB/SEM micromanipulator was sharpened using the gallium ion beam so that its point of contact with the selected particle was minimized (this also helped in detaching the particle from the micromanipulator later on). After maneuvering the micromanipulator into contact with the particle they were attached to each other by platinum deposition (Figure 4). The micromanipulator with the tin particle attached was then maneuvered towards the AFM cantilever to bring the particle into contact with the tip (Figure 5). Platinum was then deposited from behind the cantilever tip and onto the contact area with the particle in order to join the particle to the tip position (Figure 6).

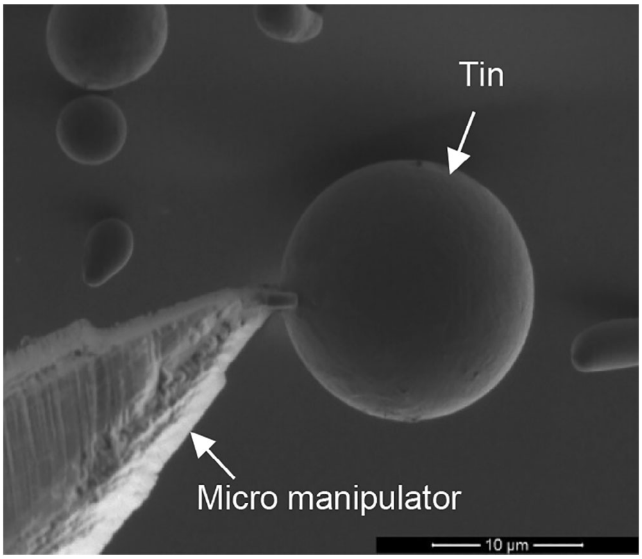

FIGURE 4 Attachment of a tin particle to the micromanipulator

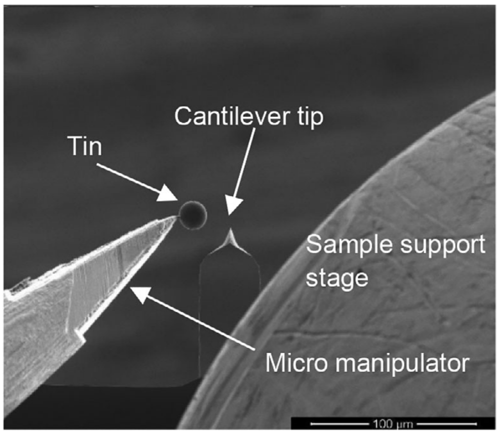

FIGURE 5 Approach of the tin particle, attached to the micromanipulator, to the cantilever tip

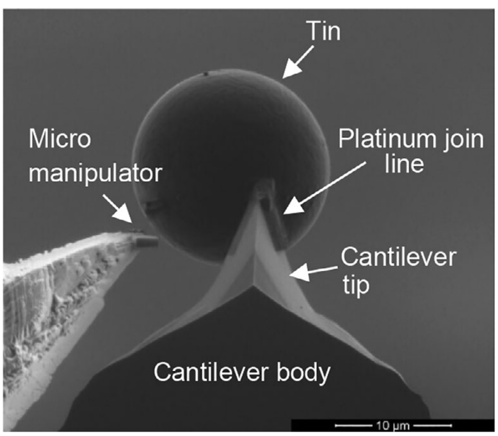

FIGURE 6 Micromanipulator detachment after attaching the tin particle to the cantilever tip by platinum deposition

Finally, the gallium ion beam was used to cut the micromanipulator away from the particle to release the functionalized tip (Figure 6). At each stage great care was taken to minimize the ion beam dose to which the particle was exposed to avoid changing its surface composition, although this was not expected to be significant as the area of the particle used for the analysis was out of the line of sight of the ion beam.

4 | DESIGN OF EXPERIMENT

The primary aim of the AFM force-distance work reported here was to establish an adhesion hierarchy among the selected polymers with respect to tin. Consequently, only relative rather than absolute measurements of adhesion force were required and it was not necessary to calibrate the stiffnesses of the cantilevers used. A careful design of experiment was required to ensure that systematic errors would not distort the results. The basic principles were: to generate a set of measurements consisting of readings from all six of the thermoplastics with the same tip in a single sitting; to generate multiple sets of measurements taken on different days and at different times of day; and, to vary the order of materials within each set. In all, three tips were functionalized and used. The cantilever deflection values at pull-off obtained from each polymer with a given tip were normalized with respect to the value obtained with the same tip for PA 6.

A number of potential systematic experimental errors were identified and mitigated. First, although all the cantilevers had the same nominal specifications, their actual spring constants would vary. Using a single cantilever over a full reading set allowed direct comparison in a single sitting between each polymer and eliminated the need to measure spring constants. In addition, the magnitude of the functionalized cantilever deflections at pull-off would also be expected to vary between cantilevers due to the difference in contact area created by different functionalizing particle sizes. However, again by using the comparison approach across the samples, this eliminated variation from this source. Repeated use of the functionalized probes could also result in wear of the particles and hence change in contact area and measured pull-off force. In order to mitigate against this the order of materials tested was changed for every set of measurements. Similarly, surface roughness may affect the results as the area of contact between the particle and the surface may change and, therefore, readings were taken from multiple areas on each polymer granule and an average was calculated. Humidity and temperature changes during the course of the tests may also affect the measurements. All the samples were dried before the experiments, however, on subsequent exposure to normal atmospheric conditions the polymers would begin to re-absorb moisture and develop a surface film of moisture. In order to reduce variation in results due to changes in atmospheric humidity, measurement runs were conducted in one sitting. A measurement run consisted of a set of readings on all six tin-thermoplastic pairs, ensuring that the humidity and temperature conditions remained approximately constant across all the samples. Also, in order to confirm that the variation in humidity and temperature did not affect the relative adhesive strengths, each run of readings was produced at a different time of day and on different days. The order in which the polymers were tested was also varied so that a systematic absorption of moisture during the course of the experiment would not affect the results. Finally, to avoid problems with processing-derived surface contamination, for example, mold release agents, polymer granules in the as-supplied state were used for the measurements and only dried according to the manufacturer's specification before use.

5 | FORCE DISTANCE MEASUREMENTS

Figure 7 shows a representative force-distance plot obtained using cantilever number 1 with PA 6; the blue line corresponds to the extend, and red to the retract phase. No clear jump to contact feature is seen in the extend plot, but otherwise the cantilever response is similar to the ideal behavior represented in Figure 2. The jump to contact feature during the extend phase of the plot varies from polymer to polymer as it occurs when the gradient of attractive forces exceeds the spring constant. The materials tested showed very little jump to contact, except ABS that showed a clear interaction, as can be seen in Figure 8

The form of the force-distance plot was consistent for measurements on a given polymer and varied between the polymers. In general, the nature of the curves was very similar to the ones reported in the literature. For most of the polymers the extend and retract curves overlapped. However, for ABS this was not the case as shown in Figure 8. This may be because of the viscoelastic nature of the materials.[17,18] The curves would be expected to overlap exactly in the case of perfectly elastic materials. However, in the case of viscoelastic materials the sample undergoes some plastic deformation during loading and it does not regain its shape during unloading. Unlike the other materials tested in this study, ABS contains a rubbery component that may affect its performance differently in the compressive and tensile parts of the trace, or it may be influenced by the presence of voids.[34]

Table 1 summarizes the results from all of the experiments. For each sitting, a single cantilever was used to measure all materials. With each material three values of pull-off deflection were obtained, measured on different parts of the granule surface. It can be seen that the results were very consistent for the same cantilever, such that the three individual values of pull-off deflection for a given material and cantilever are all within a range of 8% of the mean for that sitting.

Work of adhesion depends on the surface energies of the interacting surfaces. In the Derjaguin approximation, for the case of a spherical tip interacting with a flat

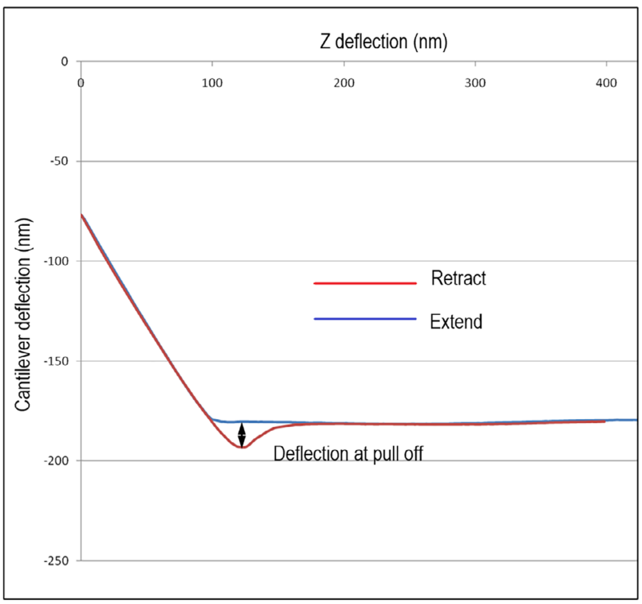

FIGURE 7 Cantilever deflection vs Z deflection for tin functionalized TESP probe and PA 6 [Color figure can be viewed at wileyonlinelibrary.com]

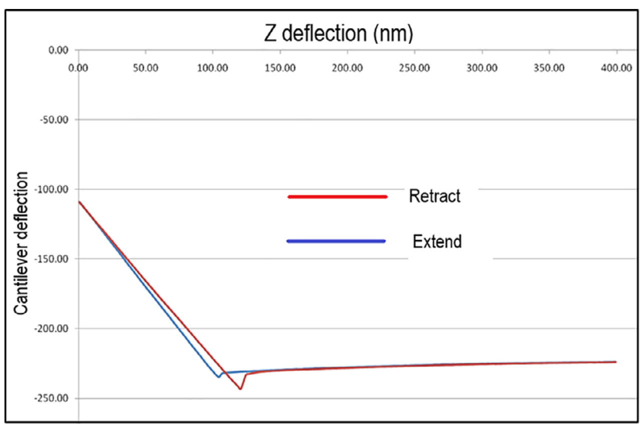

FIGURE 8 Cantilever deflection vs Z deflection for tin functionalized TESP probe and ABS [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Cantilever deflections at pull-off.

	Cantilever 1					
Material	PS	PBT	PC	ABS	PMMA	PA6
Deflection at pull off (nm)	9.3	11.2	19.9	10.4	18.1	7.9
	9.6	11.4	19.8	10.1	18.3	7.8
	9.2	11.1	20.7	10.1	17.9	8.1
Average (nm)	**9.37**	**11.23**	**20.13**	**10.20**	**18.10**	**7.93**
Ratio to PA6	1.18	1.42	2.54	1.29	2.28	1.00
	Cantilever 2					
Material	PS	PBT	PC	ABS	PMMA	PA6
Deflection at pull off (nm)	13.4	14.2	25.1	14.3	23.7	10.1
	12.0	14.6	25.6	14.4	23.6	11.5
	13.1	14.2	25.3	14.8	23.1	11.1
Average (nm)	**12.83**	**14.33**	**25.33**	**14.50**	**23.47**	**10.90**
Ratio to PA6	1.18	1.31	2.32	1.33	2.15	1.00
	Cantilever 3					
Material	PS	PBT	PC	ABS	PMMA	PA6
Deflection at pull off (nm)	13.4	18.2	28.5	16.3	26.2	11.1
	12.3	18.6	28.1	16.1	26.9	11.5
	11.7	19.2	28.3	15.8	29.5	11.1
Average (nm)	**12.47**	**18.67**	**28.30**	**16.07**	**26.53**	**11.23**
Ratio to PA6	1.11	1.66	2.52	1.43	2.36	1.00

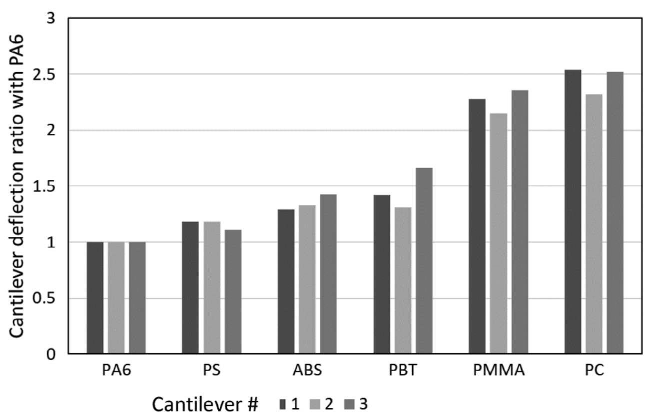

FIGURE 9 Cantilever pull-off deflection ratios (normalized to the PA 6 value)

surface, the work of adhesion, $\bar{\omega}$, is directly proportional to the pull-off force between the AFM cantilever tip (radius, R_{tip}) and sample surface (Equation 1).[17]

$$\bar{\omega} \propto \frac{F_{pull\ off}}{2\pi R_{tip}} \tag{1}$$

For the same functionalized cantilever, the tip radius will be constant and therefore the ratios of the work of adhesion between material pairs are directly given by the ratios of the cantilever pull-off deflection.

Making use of Equation 1, and in order to be able to compare the results across the different cantilevers, the averages of the cantilever pull-off deflections were normalized to the value for PA 6. For all three cantilevers the observed trend was almost the same except for cantilever 2 where ABS and PBT exchanged places. The interactions for PC and PMMA (eg, cantilever 1 normalized values 2.54 and 2.28) were noticeably stronger than for the other polymers (PS: 1.18, PBT: 1.42, ABS: 1.29, PA6: 1). It is clear that the cantilever pull-off deflections can be robustly ranked in order to understand which polymers show better surface-surface adhesion to tin. In general, the order is (strongest to weakest adhesion):

$$PC > PMMA > PBT > ABS > PS > PA\ 6$$

6 | DISCUSSION

In order to answer the question of whether the results obtained in this work, and the technique of AFM with a tin functionalized tip in general, are useful for materials selection, two considerations should be examined. The first is whether experimental confounding factors have been successfully allowed for in the methodology, so that the actual material-material interaction strengths are being measured, and the second is whether the material-material interactions determined are likely to be the same as, or representative of, those operating to secure the integrity of bonding between overmold and insert in a product with insert molded electronic components.

To assist with addressing the first question the average pull-off deflection ratios for each cantilever in Table 1 are presented graphically in Figure 9. It can be seen that while there is some overlap between values for ABS and PBT, and PMMA and PC, in general the variation between materials is greater than the variation between cantilevers for each material. It can be concluded that the experimental procedure was robust and able to differentiate between the polymers, and that the influence of material-material interactions on the measured deflection values is greater than that of the potential sources of systematic error discussed in the Design of Experiment section.

The data can also be used to approximate the relative spring constants of the three cantilevers. The force, F, corresponding to a tip deflection, δ_c is given by Equation 2, where k is the spring constant of the cantilever.

$$F = -k\delta_c \tag{2}$$

For a given cantilever (same attached particle radius) the pull-off force ($F_{\text{pull off}}$) is therefore directly proportional to the cantilever pull-off deflection (Equation 2). Using the ratios of the average cantilever pull-off deflections for PA 6 shows that the spring constants of cantilevers 2 and 3 were approximately 1.5 times that of cantilever 1. Such a direct comparison of data can be a good approximation at best, as it assumes that the particle size of each functionalized tip (and therefore the area of contact) is the same, however, it does provide a further check on the robustness of the data as the degree of variation in spring constant is within the expected manufacturing tolerance range of a factor of four.

The data from this work and the technique of functionalizing an AFM tip with a tin particle and using it to measure tin to polymer material-material interactions are therefore likely to be useful in the development of a process for electronics manufacture utilizing overmolding. Furthermore, the developed FIB/SEM technique for functionalizing the AFM tips can in principle be used for other metals where particles of the appropriate size are available. This may be of particular use where the metal concerned is an alloy, such that the bulk material composition cannot be reproduced by using a coating technique for the functionalization.

To address the second question, of whether the measurements are relevant to insert molding joint integrity, the forces likely to contribute to the material-material interaction in the AFM measurements are examined here. These forces are van der Waals forces, electrostatic forces, and capillary forces.[17,18,35] The force of interest for overmold adhesion is only van der Waals. Electrostatic and capillary forces may affect the AFM measurements but do not contribute to the strength of adhesive joints such as those in insert molding. In the AFM measurements the capillary forces arise due to a thin layer of water that normally covers most surfaces under ambient air conditions. The thickness of this layer depends upon the hydrophilicity/hydrophobicity of the surface as well as humidity. In the case of capillary forces being high the approaching tip "jumps to contact" as the tip approaches the thin water layer and a large cantilever deflection value is observed during retraction. For the six thermoplastics tested, the jump to contact was not observed except in the case of ABS which is counterintuitive as nylons in general are more hygroscopic than ABS,[35] but no such jump to contact was seen in the case of the nylon PA 6.

Electrostatic forces in AFM measurements arise from the difference in charge between tip and substrate. Certain materials become electrically charged when they come in contact with another different material and are then separated. The polarity and strength of the charges produced depends on the materials, temperature and other factors. Hearn and Ballard used this property of polymers to segregate PP, PET, PS, PVC, and HDPE from one another for recycling.[36] Diaz and Felix-Navarro compiled a triboelectric series for the polymers when tested with gold.[37] They reported that the magnitudes of the charges developed by the polymers are all of the same order, apart from nylons that are larger. They found that polymers with nitrogen functional groups (eg, ABS and PA 6) develop a positive charge. Polymers with oxygen functional groups (PMMA and PC) also develop a small positive charge, but less than the nitrogen functional group polymers. Polymers with hydrocarbons as functional groups show little charging and generally are close to 0 (PS and PBT). Thus, for the experiment discussed here, the electrostatic force should be largest for the PA 6 and of comparable magnitude among all the other polymers. In fact, PC and PMMA showed much the highest pull-off force as compared to other thermoplastics, the pull-off force for PA 6 was the least, and the pull-off forces of PS, PBT and ABS were comparable. Thus, it may be concluded that although electrostatic forces may contribute to the pull-off forces, they were not dominant in deciding the measured values and therefore the overriding material-material interaction encountered in this study was van der Waals interactions.

7 | CONCLUSIONS

As part of a larger investigation of the factors influencing the practical joint strength achieved when tin coated electronic components are overmolded with thermoplastics, AFM force-distance measurements between six commodity thermoplastics and tin were carried out. A FIB/SEM based method was developed to functionalize AFM cantilevers by attaching a tin particle to them. Highly consistent pull-off cantilever deflections were obtained (maximum range with respect to the mean of less than 8%), allowing the six thermoplastics to be robustly ranked by strength of interaction with tin as follows:

$$\text{PC} > \text{PMMA} > \text{PBT} > \text{ABS} > \text{PS} > \text{PA 6}.$$

The PC and PMMA interactions with tin were found to be noticeably stronger (by almost a factor of two) than the other polymers. From consideration of possible contributions to the pull-off forces measured, that is, van der Waals, capillary and electrostatic forces, it was concluded that the contribution due to van der Waals forces is likely to be at least significant, if not determinative.

As it is only the van der Waals forces that may influence insert to overmold joint integrity, it was further concluded that the data from this work and the developed AFM technique are likely to be useful in the development of a process for electronics manufacture utilizing overmolding. Furthermore, the technique of functionalizing an AFM tip using a FIB/SEM may be useful in a wider context of investigations of metal-polymer interaction forces, as it in principle allows attachment of metal particles of composition representative of bulk material, for example alloys.

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