

# Bulk soldering: Conductive polymer composites filled with copper particles and solder

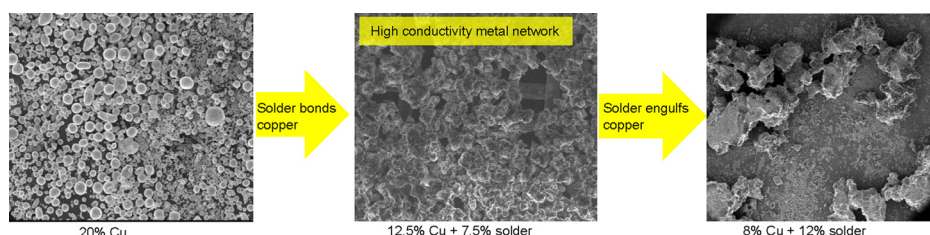


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## GRAPHICAL ABSTRACT



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## ABSTRACT

The electrical conductivity of plastics can be improved by metal filler particles, but high metal loadings (several ten volume percent) are generally needed to realize percolating pathways that can conduct electricity. We explore the improvement of the electrical conductivity of polystyrene by simultaneously adding two different metal fillers: copper particles, and a lead/tin solder alloy. The essential idea is that during mixing, the solder can bind together the particles via numerous menisci and the resulting copper-solder aggregates can then form a percolating network – hence the term “bulk soldering”. We show that this approach can realize high conductivities at total metal loadings that are far lower than if the copper particles were used as the sole conductive filler. SEM confirms that the microstructure consists of copper particles bonded by the solder, and that such aggregates can percolate throughout the sample volume. Indeed at a total metal loading of 20 vol%, the mixing process can create an all-metal scaffold that remains free-standing even when continuous phase polystyrene is removed. We examine the effect of composition on the microstructure and conductivity, and show that there is an optimal solder:copper volume ratio of roughly 0.6 which gives the highest conductivity. High conductivity is achieved only if a flux is added during mixing. The flux removes the copper oxide layer on the copper particles, and hence ensure wetting of copper by solder. Finally we comment on the similarities and differences between these polystyrene/solder/copper mixtures versus other liquid/fluid/particle mixtures in which capillarity induces aggregation of particles.

## 1. Introduction

It has been long recognized that capillary forces (i.e. forces stemming from surface or interfacial tension) can greatly affect the structure of particulate systems [1–7]. Examples include the strength of wet

granular materials which comes from particles being bound together by bridging menisci [8], “spherical agglomeration” of particles by collecting them within drops [9], particle-stabilization of foams due to strong adsorption of particles to the air/liquid interface [10–12], and the stability of “bijels” against coarsening [13]. The common feature in

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such materials is that the capillary force offers a simple means of binding together particles and hence creating some specific aggregated structure. One may then sinter this structure to make it more permanent [14–17], thus offering a processing route to new materials. The rich variety of microstructures that can be realized due to capillary phenomena in particulate materials has been reviewed recently [5,18]. Progress on using capillary forces for developing new materials has also been reviewed [3].

Perhaps the most dramatic effect of capillary forces on the behavior of particulate materials is the change in rheological properties. In the above example of granular materials, dry sand can be poured readily, whereas wet sand can be molded into sand castles [8]. The same has been observed in particulate suspensions wherein addition of oil to a particles-in-water suspension (or vice versa) gives the suspension solid-like rheology, e.g. a yield stress [19]. Such changes in rheology have been regarded as the signature of a mechanically-percolating network, i.e. capillary forces not only aggregate the particles, but the aggregates form a space-spanning network that is responsible for a very high viscosity or even a yield stress.

Just as a large-scale network can affect the viscosity, it is also plausible that other transport properties of the material might be affected. In fact, electrical conductivity is one transport property that is often strongly affected by the presence of a large-scale network. This is well-recognized in reviews [20–22] on polymers that have been rendered conductive by addition of conductive fillers such as carbon black, carbon nanotubes [23,24], carbon nanoparticles, or graphene [25]. In that literature, it is commonly observed that high conductivity arises only when the filler loading exceeds a certain threshold (percolation threshold for electrical conductivity) beyond which the filler forms a network. Much research on conductive polymer composites has sought to reduce the percolation threshold, e.g. by using high aspect ratio fillers such as conductive fibers [26,27].

The goal of this article is to examine the improvements in conductivity of a polymer due to addition of conductive filler particles which are bonded by capillary forces. Specifically, we use polystyrene (PS) as the low-conductivity matrix polymer, copper particles as the conductive filler, and a tin-lead solder alloy as the fluid that induces capillary forces between the copper particles. The essential physical picture can be illustrated in Fig. 1 (Section 2 will provide experimental support for this picture). Fig. 1a&b depicts the case of copper particles dispersed in PS in the absence of solder. Since the particles do not aggregate to a significant degree, a relatively high particle loading is needed to realize a percolating network. Moreover, neighboring particles make relatively poor contact with each other, and hence low conductivity is expected. This is because even a small separation between the particle surfaces, being filled with the low conductivity matrix, adversely affects conductivity [28,29]. Fig. 1c&d shows the effects of adding solder during the blending process. The solder, being fully-wetting towards the copper, can bridge the particles by a meniscus (Fig. 1c&d) which can lower the percolation threshold. Crucially, the capillary forces are induced by the liquid metal alloy that is itself highly conductive, thus allowing the possibility of a fully-metallic network that spans the entire sample. This idea of bonding together metal particles by mixing them with solder is dubbed “bulk soldering” in this paper.

Although the term “bulk soldering” is new, the idea of combining non-melting metal filler and low-melting point alloys (LMPA) to improve the conductivity of plastics has been explored to some extent. We have reviewed the broad literature on LMPA-polymer composites recently [30] and cite four papers [31–34] which melt-blend LMPA, non-melting metal filler, and polymer. The LMPA used in those articles were typically alloys of metals such as tin, lead, and bismuth, and had melting temperatures below 250 °C. The LMPA, the non-melting metal filler, and polymer were all blended at a temperature above the LMPA melting point. This approach has two advantages: standard plastics processing equipment may be used for blending (and hence the

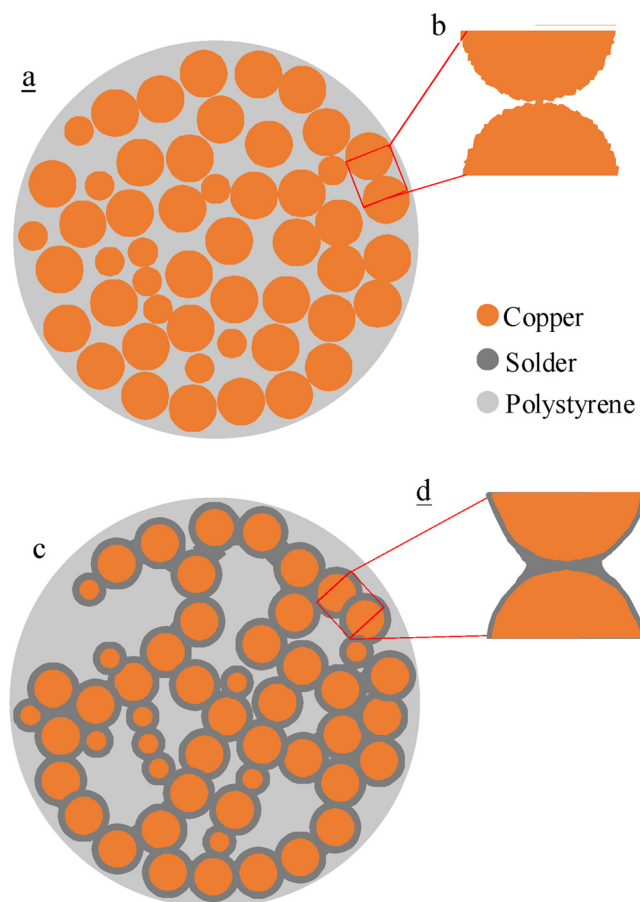


Fig. 1. Schematic of (a) Copper dispersed in polystyrene without flux and solder to form polymer composite (b) magnified view of a particle-particle contact (c) copper and solder in polystyrene forming metal network (d) magnified view of solder bonding particles via a meniscus.

manufacturing approach is readily scalable), and the resulting blends can have high conductivity. A somewhat different example of this approach is from Sun et al [35,36] who used a cross-linkable epoxy matrix and silver particles that were bonded by an ionic liquid (rather than a liquid metal), although the amount of ionic liquid was only a small fraction of the particle loading.

Obviously for practical applications as conductive plastics, it is desirable to achieve high conductivity at as low a metal loading as possible. Much of the previous research used fairly high metal loadings: 40 vol% in Yang et al [34], 53 vol% in Zou et al [32], and over 50% in Mrozek et al [31]. Due to the relatively high cost of the metals (especially solders) as compared to plastics on a volumetric basis, these high loadings entail a high cost. Moreover, if the particulate metal is present at high volumetric loading, this also causes poor processability, as true for all particle-filled polymers. One may use lower metal loadings using high aspect ratio particles [27,33,35], but typically high aspect ratios also tend to significantly worsen processability. Yet, the literature on capillary effects in particulate materials suggest that mechanical percolation can appear at far lower particle loadings. For example, our own research on blends of particles and two immiscible polymers suggests that when particles are bridged by menisci such as shown in Fig. 1c&d, percolation (judged rheologically) can appear when the particle loading is well under 10% loading [37]. Similar research in oil/water systems [38,39] also suggests that percolation can occur at particle loadings much lower than those used in LMPA-based composites [31,32,34]. As long as the particles are separated from each other, mechanical percolation does not necessarily induce electrical percolation. However, if the particles may be bridged by a meniscus, it may be possible to induce

electrical percolation at roughly the same particle loading as mechanical percolation. We speculate that the previous studies [31,32,34] have examined only a very limited range of the composition space, and it is possible that with a more systematic study of compositional effects, high conductivity may be achieved even at a particle loading that is much lower than examined previously. In summary, the motivation of this paper is to develop the idea of bulk soldering more systematically across a wider range of composition space than examined previously, with a particular focus on lowering the metal loading needed for realizing high conductivity.

Our research approach in this paper is heavily influenced by recent research, including from our own group, elucidating structure-composition relationships in ternary liquid/liquid/particle mixtures [5]. These include a wide variety of ternary mixtures of oil/water/particles, air/water/particles, and particle-filled blends of molten polymers. Since PS/solder/copper blends constitute liquid/liquid/particle mixtures, many of the insights drawn from the previous research are directly applicable to this research. Two insights are especially relevant. The first is the importance of the relative wettability of the particles towards the two liquids. In the present case, the copper particles are fully-wetted by solder and hence – if there is sufficient solder – the particles can be engulfed by the solder completely. Thus, the solder:copper volume ratio, which determines whether engulfment happens or not, is a critical parameter determining structure. The second is the recognition that continuous metallic pathways can be created throughout the sample by three distinct microstructures (Electronic Supplementary Information - ESI Fig. S1) that correspond to different regions of the ternary composition space [40]. Any one of these pathways should have a high conductivity, however, Fig. 1c corresponds to one such pathway that creates metallic pathways via a metal-solder composite structure.

The outline of this paper is as follows. Section 2 first describes the materials and methods briefly (details in ESI), followed by experimental results on how the conductivity and microstructure are affected by total metal loading (Section 2.2), the critical role of flux (Section 2.1), the solder:copper ratio (Section 2.3) and copper particle shape (Section 2.4). Section 3 discusses the results, especially in regard to how these ternary mixtures compare with in oil/water/particle or polymer/polymer/particle mixtures examined previously.

## 2. Results

Samples were prepared from polystyrene (PS), 30–80 micron diameter copper particles (ESI Fig. S2), and “solder paste” of a grade typically used in the microelectronics industry. The paste consisted of 15–25 micron diameter particles of Sn<sub>63</sub>Pb<sub>37</sub> dispersed in a continuous phase flux. The melting point of the Sn<sub>63</sub>Pb<sub>37</sub> is known to be  $T_m = 183$  °C. Most samples also included a solder flux to clean the particles (see below). Other details of the materials are given in the ESI.

Samples were prepared by blending all components under molten conditions, first mixing the copper particles and the flux, then adding the solder paste, and finally the PS. The temperature during the last mixing step was 220 °C, far above the melting point of the solder particles. All other details of mixing are given in the ESI.

The samples were molded into discs at 225 °C and conductivity measured through the thickness. The surface of the discs was sanded lightly to expose the metal particles and ensure good contact with electrodes. Samples were also immersed in toluene to extract the PS, upon which the metal dispersed phase could be recovered and imaged by optical and electron microscopy. All the details of conductivity and structural characterization are given in the ESI.

The composition of the samples is specified by two volume fractions  $\phi_{\text{solder}}$  and  $\phi_{\text{copper}}$  (the polystyrene being the remainder). We will frequently refer to the volume ratio of the solder to the copper as  $\varphi$ :

$$\varphi = \frac{\phi_{\text{solder}}}{\phi_{\text{copper}}} \quad (1)$$

Two series of samples were prepared: the first that varied  $\phi_{\text{solder}}$  and  $\phi_{\text{copper}}$  keeping  $\varphi$  fixed at 0.15 (Section 2.1 and 2.2) and the second that varied  $\varphi$  at a fixed metal loading of 0.2 (Section 2.3). In most of our previous research on the fundamentals structure-composition relationships, the composition of liquid/liquid/particle mixtures was represented on a triangular composition diagram. Analogously, the compositions of all the three mixtures are shown on such a diagram in ESI Fig. S6.

Initial experiments were conducted at a single solder:copper ratio of  $\varphi = 0.15$ . The rationale for selecting this ratio is guided by analogous research on other liquid/liquid/particle ternary mixtures. That rationale is as follows. As mentioned in the Introduction, since the solder can wet the copper completely (see below), we anticipate that solder and copper will form a combined phase in which copper particles are dispersed in solder. Such a combined phase is expected only if the solder volume is adequate to completely engulf all the particles. The schematic picture of Fig. 1c&d requires the solder to join the particles either pairwise or via a few-particle contacts, but not complete engulfment. Previous research suggests that in analogous ternary mixtures when the particles are fully-wetted by one phase, complete engulfment requires the wetting phase to be roughly 25% of the volume of the particles [5]. Thus a  $\varphi$  value of 0.15 seems suitable to avoid complete engulfment, and hence this value was adopted for initial experiments. Later experiments also examined  $\varphi$  values ranging from 0.06 to 1.5.

### 2.1. Critical role of flux

Fig. 2 compares the electrical conductivity at several filler loadings for three different sample families. The lowest set of data (filled triangles) correspond to polymer-copper composites prepared by simply dispersing copper particles (as received) into polystyrene. These samples have low conductivity even at 30 vol% copper loading. One reason for this low conductivity is simply that the copper particles are well-separated by an insulating layer of polystyrene. Yet a second reason may be that copper is generally covered with a thin surface layer of oxide which is insulating. Thus, even when two particles make physical contact, there may still be an insulating oxide layer preventing good electrical contact.

Accordingly, samples with the same copper loading were prepared, but with the particles being pre-dispersed into flux prior to blending with polystyrene. The resulting samples (open red circles in Fig. 2) were found to have a conductivity that was orders of magnitude higher. These experiments testify to the importance of having metal surfaces

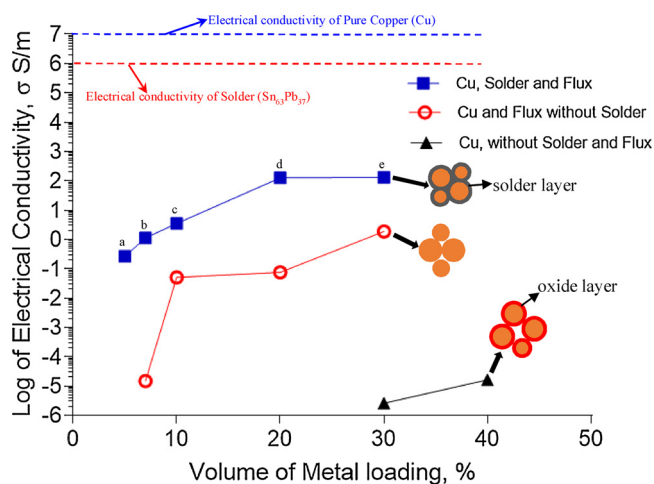


Fig. 2. Conductivity of PS/solder/copper composites at various total metal loadings where  $\varphi = \phi_{\text{solder}}/\phi_{\text{copper}}$  was kept fixed at 0.15. The points labelled a, c, d and e refer to the corresponding images in Fig. 3 which shows morphologies of these samples.

that are extremely clean: it appears that oxide film poses a significant resistance to electron conductivity, and removing it can increase conductivity.

Flux has two important constituents called *activators* and *vehicles* [41]. Information provided from the flux manufacturer shows that the activators in the flux used here are  $\text{NH}_3\text{Cl}$  and steric acid. The former can readily decompose at high temperature to produce HCl. Both acids can reduce the CuO layer on the particles. The vehicle (i.e. the carrier phase) for this specific flux is not known, but often includes a solvent, and possibly some non-volatile species.

Weighing experiments on the samples before and after mixing suggest that roughly half of the mass of the flux is volatile and is lost during the melt blending process. A separate experiment conducted with a mixture of flux and polystyrene (no metal) shows that the non-volatile portion remains in the sample in the form of a dispersion. In samples that contain solder and copper particles (discussed in the next section), due to opacity, our experiments are not able to determine the location of the non-volatile portion of the flux. Yet, the fact that the copper is well-wetted by the solder suggests that they do not interfere with the wetting of copper by solder.

## 2.2. Bulk soldering of copper particles

We now turn to samples to which solder is added, and this section is restricted to samples for which  $\varphi = 0.15$ . Fig. 2 shows that these samples have far higher conductivity than the flux-containing samples without added solder. We emphasize that the x-axis of Fig. 2 is drawn at total metal loading, i.e. the conductivity increase occurs not because adding solder raises the metal loading, but because the solder changes the microstructure.

We examined the microstructure directly by Scanning Electron Microscopy (SEM) after removing the PS phase by selective dissolution in toluene. In the absence of solder, the copper particles are well-wetted by PS, as may be judged by their good dispersion. Dissolution of the PS phase gave a slurry of copper particles in toluene indicating that the copper particles were completely separated. With addition of solder, the copper particles were found to be bonded together into aggregates (Fig. 3a). The aggregate size increased with total metal loading (Fig. 3b-

f) until, at 30 vol%, the solder-copper together formed a fully-self-supporting scaffold that retained the original shape of the molded disc (Fig. 3e). In fact, a large-scale scaffold was evident at 20 vol% as well (Fig. 3d), although it was fragile and fragmented upon extracting from toluene. It is the presence of this very open scaffold that provides highly conductive pathways throughout the sample and hence is responsible for the high conductivity.

Higher magnification views (Fig. 3c and f) show the details of the particle contact and confirm that the solder wets the particles. Indeed, complete wetting is evident even without any SEM at all: when a blend such as Fig. 3b is immersed in toluene, the remaining metal aggregates appear to be a dull silvery color (Fig. S4d) rather than the red color of copper (Fig. S4a&c). This indicates that the solder is not only bonding together copper particles, but also covers the copper surfaces. Yet, the microscopic picture of particle contact (Fig. 3c) appears to be more complex than Fig. 1d. Specifically, the contacts between the particles are not strictly pairwise as sketched in Fig. 1d, but instead involve multiple particles bonded together by a single meniscus. Such a microstructure was dubbed “pendular/funicular morphology” in our research [5,9] on immiscible liquids with particles. These images suggest the schematics drawn alongside each set of data in Fig. 2, with two features being noteworthy (1) particles in the lowermost schematic are depicted with an oxide film, which is no longer present in the middle schematic (after flux treatment), and (2) in the uppermost schematic, the space between the particles is depicted as filled with solder.

Finally, we re-emphasize the critical role of the flux in creating the solder-bonded particle structure. In the absence of flux, the solder by itself is ineffective in raising conductivity. Specifically, a limited number of PS/copper/solder mixtures were prepared by simply melt-blending dry solder powder, copper particles (as received), and PS. These blends had low conductivity suggesting that the copper particles are not well-wetted by solder in the absence of flux. To verify this, we compared the melting behavior of solder on copper foil without and with flux. If dry solder powder was placed on copper foil and melted (Fig. S5a), it coalesced into large blobs which, upon cooling, were easily chipped off the surface of the foil (Fig. S5b). In contrast, melting the solder paste (which is the same solder particles dispersed in flux) on foil resulted in excellent wetting (Fig. S5c) and it was not possible to chip

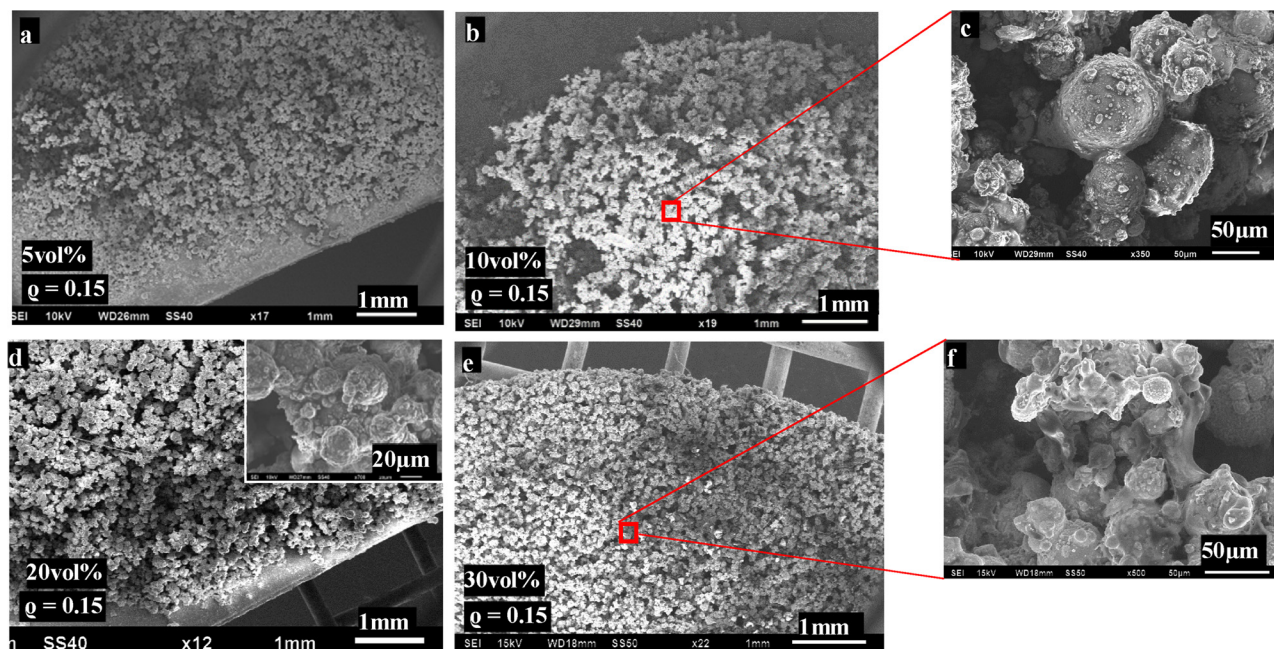


Fig. 3. SEM images of conductive polymer composite with copper particles, solder, and flux. Samples are prepared at constant  $q$ -value of 0.15 with increasing total metal loading after selective dissolution of polymer matrix (PS) with metal loading of (a) 5 vol% (b) 10 vol% (d) 20 vol% and (e) 30 vol% show low magnification images with (c and f) at high magnification of 10 vol% and 30 vol% metal loading respectively.

away the solder from the foil (Fig. S5d), making it easy for the solder to wet the surface of the copper [42,43]. Thus, the removal of oxide from the copper surface is a critical step in realizing high conductivity.

To our knowledge, there is no prior research on adding flux to improve the conductivity of metal-filled plastics. This idea is potentially applicable not only to copper, but also to other metals that are used to improve the conductivity of plastics. Indeed, specialized solders are available even for making the surface of stainless steel suitable for soldering, and this may be a useful method to improve the conductivity of conductive plastics based on stainless steel fibers [44]. The chief challenge is that such fluxes are corrosive and may be damaging to processing equipment.

### 2.3. Effect of solder:copper particles ratio on composite

We now examine the effect of the solder to copper ratio,  $q$ . As mentioned in Section 2.2 when the particles are fully-wetted by one of the two liquids, two possibilities arise depending on the wetting fluid:particle ratio. If the  $\varphi$  value is sufficiently large, the particles and the wetting liquid form a combined phase. In contrast, if the  $\varphi$  value is relatively small, the wetting liquid tends to form menisci that bond the particles together. Accordingly,  $\varphi$  strongly affects microstructure, and in the present case, is likely to influence conductivity. Indeed this was noted by Zou et al. [32] albeit at a very high metal loading (53 vol%), and by Sun et al. [35] in an ionic liquid system, although these latter experiments used highly non-spherical particles and relatively small  $\varphi$  values. Here we re-examine this question, but at a much lower metal loading (20 vol%) than Zou et al. [32], and across a range of  $\varphi$  values that span the expected transition from meniscus-bound to a particle-engulfed state. Since the total metal loading is held fixed at 20%, these sets of samples trace a trajectory in the triangular composition space that corresponds to  $\phi_{PS} = 0.8$  as illustrated in Fig. S6, and in Fig. 4f. Practically this trajectory is interesting because it may be possible to improve the conductivity without increasing the metal loading, but by choosing a  $\varphi$  value different from the  $\varphi = 0.15$  used in Figs. 2 and 3. But conceptually as well, varying the solder:copper ratio is interesting since it allows a direct comparison of this system against the previously-constructed map of microstructure across a wide range of compositions for model polymeric systems [9,40,45]. Specifically, we showed that as

the volume fraction of the particle-wetting fluid was increased, there was a sequence of structural transitions from meniscus-bound particle aggregates to capillary aggregates to phase inversion, sometimes with an intermediate cocontinuous morphology. In this section we will test whether similar structural changes appear, and how they affect conductivity.

Fig. 4 illustrates the effect of changing  $\varphi$  at a fixed total metal loading of 20 vol%. Fig. 4a corresponds to the lowest solder content of  $\varphi = 0.06$ , which corresponds to  $\phi_{solder} = 1.1\%$  and  $\phi_{copper} = 18.9\%$ . As expected at this relatively low solder content, there is insufficient solder to engulf the copper particles completely. Accordingly, the sample dispersed completely upon immersing in toluene, and SEM revealed discrete aggregates of few copper particles bonded by menisci of solder. Fig. 4b (identical to Fig. 3d) corresponds to  $\varphi = 0.15$ . As mentioned above, upon removing the PS, all the metal was consolidated into only a few large fragments which are called a pendular/funicular network of the filler phase. With further increase in the  $\varphi$  value to 0.6 (Fig. 4c), all the particles became bonded into a single percolating network, and immersing the sample into toluene gave a single porous disc of metal. In SEM, the particles appear to be heavily covered with solder and strongly bonded into large aggregates. A further increase in  $\varphi$  to 0.9 (Fig. 4d) led to significant coarsening of the morphology. While a large and fairly open network still exists at this composition, the size-scale of the “building block” of this network is no longer a single particle, but large blobs of particles held together by solder. Previously, we called these blobs “capillary aggregates”, and the corresponding network as a “capillary aggregate network”.

A further increase in  $\varphi$  to 1.5 (Fig. 4e) leads to a breakdown of the percolating network. This can be anticipated based on our previous research [9,45] and can be explained readily: capillary aggregates are stable against coarsening because they have a very high internal volume fraction of particles, e.g. at  $\varphi = 0.9$ , the copper particles constitute 53 vol% of the combined (copper + solder) phase. At such a high-volume fraction, the combined (copper + solder) phase is expected to have solid-like rheology, and hence cannot coarsen. When  $\varphi$  increases, the combined phase becomes dilute (e.g. Fig. 4e has only 40% copper in the combined phase). Due this dilution, the combined phase behaves like a relatively low viscosity liquid and can coalesce or breakup readily. Under these conditions, sustaining a network is difficult due to

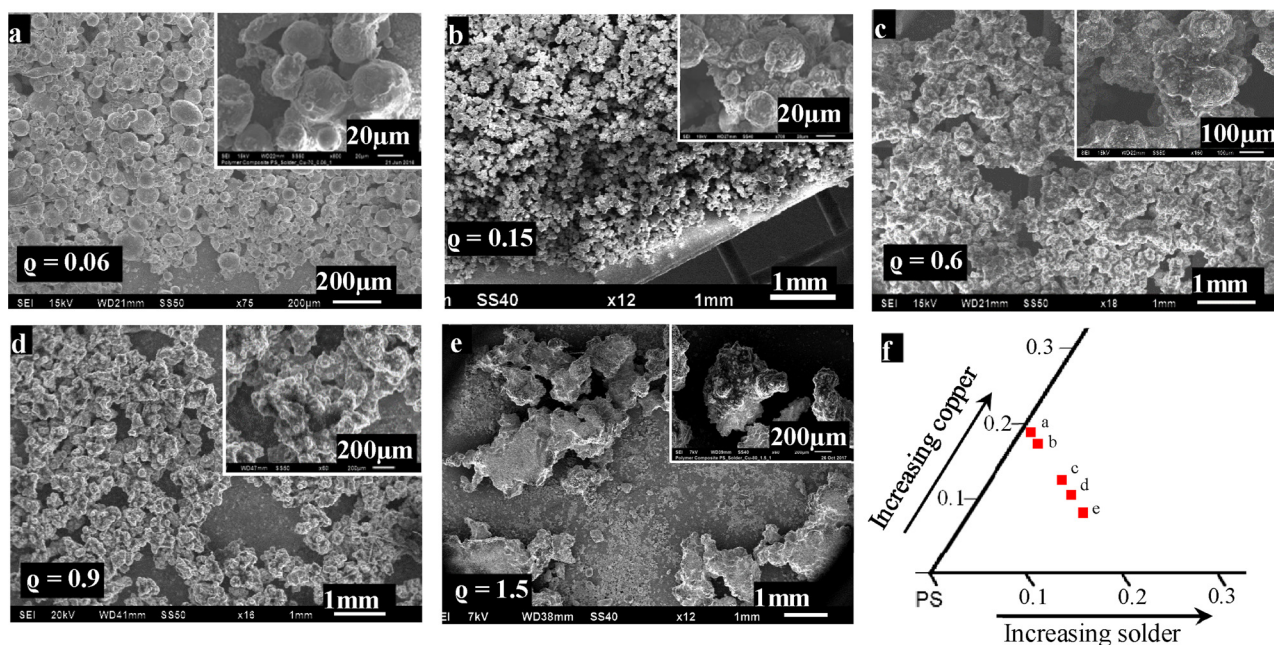


Fig. 4. SEM images of conductive polymer composites with copper, solder and flux at different  $q$ -values at fixed metal loading of 20 vol%. The triangular composition diagram shows the compositions of the samples shown in Fig. 4a–e.

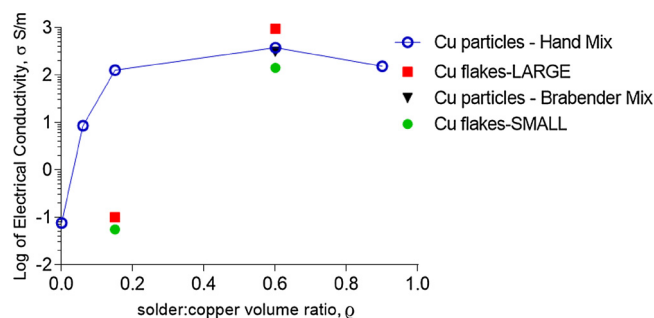


Fig. 5. Conductivity of polymer composites with 20 vol% metal loading at different  $\phi$ -values. Several sizes and shapes of copper particles were used in preparing composite samples and tested.

rapid coarsening induced by interfacial tension [40].

One may expect these changes in microstructure to induce significant changes in electrical conductivity and indeed, Fig. 5 shows a sharp increase in conductivity at small values of  $\phi$ , with the  $\phi = 0.6$  giving the highest conductivity amongst the measured samples. There is clearly an optimum in the solder:particle ratio: not only does the conductivity reduce when  $\phi$  rises to 0.9, but the microstructure of Fig. 4e is so coarse that it is not possible to make homogeneous discs for conductivity measurements.

#### 2.4. Shape and mixing effects

High aspect ratio fillers, for example, acicular, fiber-like, and plate-like particles can generally percolate at much lower volume fraction than spherical particles and hence can give higher conductivity. Indeed conductive polymer blends that use stainless steel fibers as the conductive filler have been commercialized [44,46]. We examined whether replacing the spherical copper particles with flakes would affect conductivity. Flakes were prepared by ball-milling the spherical copper particles, and their morphology is shown in ESI Fig. S3. Fig. 5 compares the conductivity of four blends (two different flake sizes at two different  $\phi$  values) against the corresponding samples with spherical particles. Surprisingly, increasing the aspect ratio did not necessarily increase conductivity. At  $\phi = 0.15$ , the conductivity reduced sharply indicating a loss of the percolating network, and indeed immersion in toluene caused a complete disruption of the disc specimens. In contrast, percolation was maintained at  $\phi = 0.6$  and high conductivity was retained. The corresponding images are shown in Fig. 6. The possible reasons for this are discussed in Section 3 below.

Finally, all the research thus far was conducted by mixing by hand with a spatula. For any practical applications, the use of conventional plastics processing equipment to prepare such samples would be needed. We conducted a single experiment using a Brabender Plasticorder, a batch mixer that is commonly used in the plastics processing community. The results of this blending (Fig. 5) were roughly

comparable to those of hand-blending: the sample was found to retain a percolating network upon dissolution and had high conductivity, thus indicating that in principle, bulk soldering is viable even using standard plastics processing equipment.

### 3. Discussion

Three aspects of the experimental results deserve further discussion: a comparison of the morphologies against previous research, the behavior of the non-spherical flakes, and a comparison of the conductivities found here against those in the previous literature on combining particles and liquid metals in thermoplastic matrices.

As mentioned in the Introduction, this research was strongly influenced by previous studies of the microstructure-composition relationships in analogous oil/water/particle or polymer/polymer/particle systems [3,5,18]. The system studied here behaves in a qualitatively similar fashion, at least with changes in the solder:copper ratio. At the lowest  $\phi$  value studied here, the pendular/funicular morphology (i.e. two or just a few particles bound by menisci of the wetting fluid) appears as was also noted previously [3,5,18]. With increasing solder content, there was adequate solder to fully engulf the particles and form a combined phase highly filled with copper particles. This combined phase is expected to have solid-like rheology and hence takes the appearance of irregular lumps which we previously called capillary aggregates [47,48]. With a further increase in solder, the sizescale of the combined phase increased sharply as the combined phase starts to behave as a “normal” fluid phase capable of rapid coalescence [47,48]. Previously we also noted non-monotonic changes in rheology: the solid-like behavior of the mixtures peaked at an intermediate value of  $\phi$  corresponding to a pendular/funicular morphology [36,37]. It is more difficult to conduct rheometric experiments in the present situation, however qualitatively, the mixtures show similar rheological trends. This is illustrated in Fig. S7 where samples with various solder:copper ratios (all at fixed metal loading) were allowed to melt. It is clear from those images that the samples with low or high values of  $\phi$  sag under gravity, whereas  $\phi = 0.6$  corresponds to a relatively high stiffness for which the sample does not flow. Indeed, at the highest  $\phi$  value in Fig. S7, the size of the combined phase is so large that the PS separates from the metal phase altogether and leaves the sample.

Despite the qualitative similarity of the current system as compared to the previous liquid/liquid particle mixtures, two differences must be pointed out. The first is a quantitative difference between the  $\phi$  values at which various microstructural transitions appear. In our own studies of immiscible polymer blends with spherical silica particles that are fully-wetted by one phase [9,37,45], the pendular/funicular morphology appeared for  $\phi < 0.4$ . Capillary aggregates appeared around  $\phi = 0.6$ . For  $\phi$  values exceeding 1, the combined phase had a smooth interface indicating that the combined phase was liquid-like. These specific values of  $\phi$  refer to our own research on immiscible polymer blends with spherical silica filler, but very similar observations have been made in oil/water/particle or air/water/particle mixtures [5].

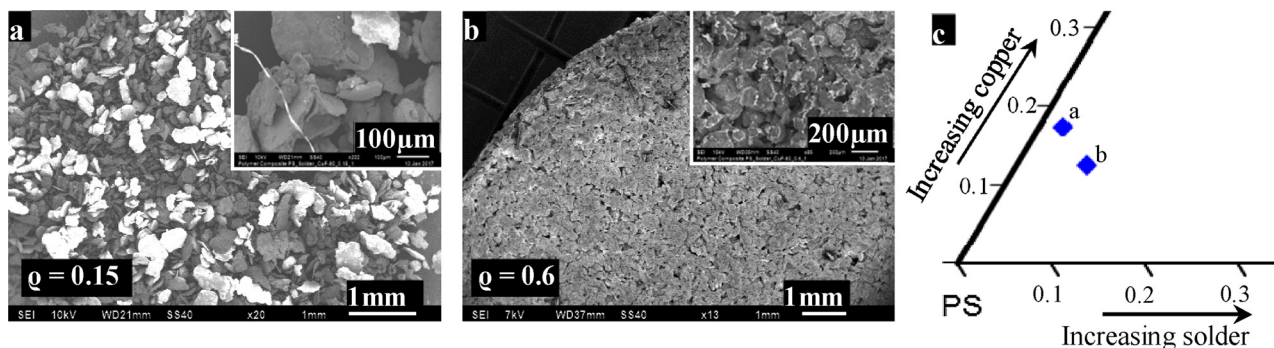


Fig. 6. SEM images of conductive polymer composite with copper flakes, solder and flux at different  $\phi$ -values.

A glance at Fig. 4 suggests that the same sequence of transitions is shifted to higher  $\varphi$  values in the PS/solder/copper mixtures. For instance, Fig. 4c (with  $\varphi = 0.6$ ) suggests that capillary aggregates are not well-developed; instead the largest aggregates still comprise solder menisci that bind just a few particles. In contrast, at a similar value of  $\varphi$ , well-developed capillary aggregates were noted previously [9,37]. Similarly, Fig. 4e shows irregular lumps indicative of capillary aggregates, whereas this  $\varphi = 1.5$  was previously found to give a smooth liquid/liquid interface in particle-filled polymer blends indicating that the combined phase behaved like a liquid [40]. We believe that the reason for this shift in the composition at which these morphologies appear is that the copper and solder react with each other. In the previous studies of polymeric materials or in studies of oil/water/particle mixtures, the combined phase was simply a *physical* mixture of the wetting fluid and the particles. In contrast, in the present case, copper is known to react with the tin in the solder to form intermetallic compounds  $\text{Cu}_3\text{Sn}$  (in the form of thin sheets) and  $\text{Cu}_6\text{Sn}_5$  (in the form of scallop-like structures) [49]. This reaction occurs by diffusion of the molten tin into copper, and the resulting intermetallic compounds are responsible for the excellent adhesion of copper and solder. Previous research suggests that this process can happen rapidly (less than 1 min) [49] and hence may indeed be relevant to our samples.

To test for the possibility of intermetallic formation, we conducted SEM imaging of the cross-section of the metal phase; in contrast, Figs. 3,4, and 6 show only the surface of the metallic phase. The sample with  $\varphi = 0.6$  was chosen for this purpose for convenience of imaging. A molded disc of the sample was polished to expose the cross section of the metal, and the corresponding images are shown in Fig. 7. In the absence of reaction, only three distinct gray levels corresponding to three distinct compositions would be expected: polystyrene (darkest), copper, and solder (brightest). Fig. 7 however shows four gray levels, and based on the expected elemental compositions, we anticipate the following sequence polystyrene (darkest), copper, tin-rich phase, lead-rich phase (brightest). To further confirm intermetallic formation, elemental analysis was conducted by energy-dispersive x-ray spectrometry, and the corresponding results are shown ESI Fig. S8. These results clearly show that in the region immediately adjacent to the copper particles where grayscale is intermediate between the particles and the meniscus, there is nearly equal copper and tin, but no lead. Moreover, the region far away from the copper particles (brightest grayscale) is depleted in tin as compared to the original solder composition. Both these strongly support the formation of copper-tin intermetallic compounds. The immediate implication is that after some mixing time, a portion of the wetting fluid (tin) turns into a solid intermetallic, thus reducing solder:copper ratio  $q$  below its value at the beginning of the mixing process. This reaction can explain, at least qualitatively, why the microstructural transitions occur at higher  $\varphi$  value as compared to analogous non-reacting systems.

It is also noteworthy that a cocontinuous structure of the type

shown in Fig. S1c has not been identified in our research. This structure consists of two phases (one with particles and one without), both of which are continuous. Unlike in Fig. S1b, in Fig. S1c, the particle-containing phase is relatively dilute in particles so that it has liquid-like rheology, and hence the interface is smooth. Although we have not seen such a smooth-interface morphology yet, it is possible that higher  $\varphi$  values and higher total metal loadings may yield such a structure. Indeed such a morphology was seen by Mrozek et al [31], albeit at metal loadings exceeding 50 vol%.

The second difference is the observation that the conductivity of the samples based on copper flakes is not significantly different from that of spherical particles. It is generally accepted that conductive fillers with high aspect ratios are beneficial because they tend to percolate at lower filler loadings. This is the reason why fillers such as carbon nanotubes, carbon nanofibers, graphene, or stainless steel fibers have attracted attention for conductive polymer composites. Yet, in the present case, only the large copper flakes gave a significantly higher conductivity than the corresponding spherical particles at the same composition. We speculate that there are two reasons for this. The first is that the large surface area of flakes require more solder to wet completely. Thus, at a given  $\varphi$  value, the solder loading may be adequate to cover the spherical particles completely, but not adequate to cover flakes of small size. The same may be true for flux as well: the amount of flux may be insufficient to fully clean the flakes. The second possibility is that capillary menisci are highly effective with flat particles, i.e. if two flat particles interact side by side, then, they will bond strongly with a meniscus. Not only is the corresponding solder “lost” (since it cannot participate in forming a network), but furthermore, the two flat particles now behave effectively like a single thicker particle. These speculations suggest that by adjusting the  $\varphi$  value, flakes may prove to be more effective at building a network. A further excellent discussion of the effect of particle shapes can be found in Maurath et al [50].

Third, the question underlying this research was whether, with a systematic study of compositional effects, a range of compositions may be identified that give high conductivity even modest metal loading. Detailed comparisons against published data are difficult because of differences in metal loading and in particle shape. The most suitable comparisons are against the two papers [31,32] that used roughly spherical particles along with liquid metal. Mrozek et al. [31] reported a conductivity of 10 S/m at 30 vol% metal loading. Mrozek et al also reported far higher conductivity exceeding  $10^4$  S/m, but at a total metal loading of 50% or higher at which the metal and the polymer were both continuous. A second comparison may be made against Zou et al. [32] who reported a far higher conductivity, roughly  $2.5 \times 10^6$  S/m at a total metal loading of 54%. Our own values from Figs. 4 and 5, are typically several hundred S/m, much higher than reported by Mrozek et al [31] at a comparable loading, but much lower than of Zou et al [32], who had a much higher metal loading.

Moving beyond spherical particles, three further articles are worth

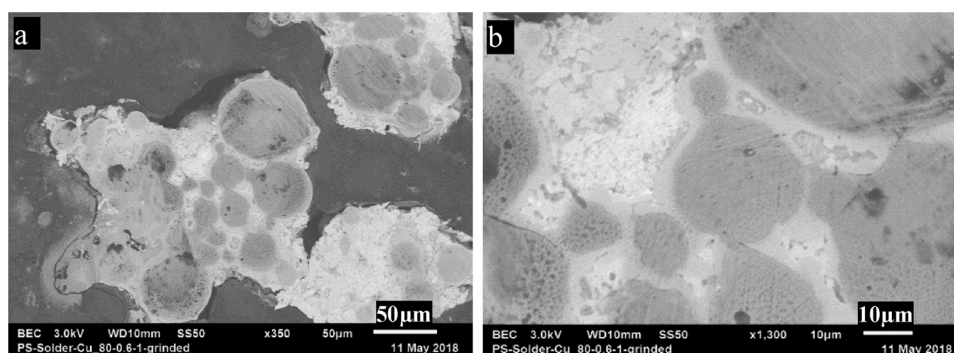


Fig. 7. SEM images of the polished cross sections of the composites. Note the gray region adjacent to the particles which indicates formation of an intermetallic compound.

mentioning although they are not comparable to our current research since they use highly non-spherical particles. Michaeli et al. [33] and Wu et al. [27] both used long copper fibers bonded together by low-melting metal. Wu et al. report a conductivity exceeding  $10^3 S/m$  at 10% metal loading. Michaeli et al. report a conductivity of  $\sim 1 S/m$  at 20% metal loading, but it rose rapidly and exceeded  $10^5 S/m$  at 40% metal loading. Finally, Yang et al [34]. used dendritic copper particles in conjunction with tin. The highest conductivities reported were about  $4 \times 10^5 S/m$  at 40 vol% metal loading although this required many hours of annealing.

It is noteworthy that the conductivity of eutectic tin-lead solder is roughly  $7 \times 10^6 S/m$ . Almost all of the reported values in the previous two paragraphs are far lower, even though many of these articles show that the metal forms a continuous phase. An exemplary case is from Mrozek et al. [31], who clearly show a continuous metal phase at 60% metal, yet report a conductivity that is almost 100-fold lower than the corresponding solder. The reason why so many researchers find a surprisingly low conductivity, even when the metal phase is continuous, remains unclear. The sole exception is Zou et al. [32] which is a far outlier: their reported conductivity of  $2.5 \times 10^6 S/m$  is only 3-fold lower of pure solder. Even more surprising, the same article reported that copper-in-polymer (without any liquid metal) had roughly the same conductivity – an unprecedented value for metal-filled plastics. Finally, they also reported that bonding copper together with solder lowered the conductivity which is surprising considering that there was excellent morphological evidence of 3D network formation.

Finally we emphasize that, in common with other liquid/liquid/particle mixtures, mixing method may play a role in structure development. For instance, limited experiments early during this research showed that pre-dispersing the solder into the PS and then adding the copper particles during blending gave a highly heterogeneous structure because the solder had coalesced into large drops even before the copper was added. This is similar to our observation that in oil/water systems [48] or in polymer systems [47], if one starts with a droplet-matrix system and adds particles that are wetted by the drops, capillary aggregates form readily. Thus, other mixing protocols or the use of higher rate mixing equipment, may improve or worsen the conductivity.

#### 4. Concluding remarks

In summary, we have developed conductive thermoplastic polymer composites based on blends of polystyrene, molten solder, and copper particles. The essential idea, which is inspired by analogous research on other liquid/fluid/particle systems, is to bind together copper particles using menisci of the solder, thus creating an all-metallic percolating network with high conductivity. Since such binding of the copper particles using solder is achieved by simply blending under molten conditions, this approach is dubbed “bulk soldering”.

We examine the effect of composition on the microstructure and conductivity, and show that even at a total metal loading of 20 vol%, it is possible to create an all-metal scaffold that percolates throughout the sample. Moreover, the solder:metal volume ratio is a critical parameter determining the microstructure and conductivity of the composites. Specifically, if this ratio is small (e.g. 0.2), the copper particles aggregate due to the solder, but do not percolate. If the ratio is large, e.g. exceeding 1, the solder engulfs the metal particles and forms a combined copper-in-solder phase that is too liquid-like to remain percolating. The changes in microstructure with ternary composition broadly resemble that of other liquid/fluid/particle mixtures, although at least some of the structural transitions require a higher ratio of solder:copper than expected from previous research. While most of the results of this paper were realized with samples prepared by hand-blending, a single test using standard plastics processing equipment shows similar results.

Finally, our results show the critical role of flux in realizing high electrical conductivity. Copper particles generally have an oxide layer,

and it is only after this oxide layer is removed that the solder can effectively wet the particles and achieve bulk soldering.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.colsurfa.2018.06.013>.

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