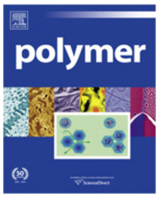
Polymer 51 (2010) 2954–2958

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Polymer Communication

Highly conductive, melt processable polymer composites based on nickel and low melting eutectic metal

Randy A. Mrozek [a,b,*], Phillip J. Cole [b,c], Lisa A. Mondy [b], Rekha R. Rao [b], Lothar F. Bieg [b], Joseph L. Lenhart [a,b,**]

[a] *U.S. Army Research Laboratory, Aberdeen, MD 21005, United States*
[b] *Sandia National Laboratories, Albuquerque, NM 87185, United States*
[c] *Northrop Grumman A&AS, Arlington, VA 22209, United States*

ARTICLE INFO

Article history:
Received 22 February 2010
Received in revised form
26 April 2010
Accepted 29 April 2010
Available online 7 May 2010

Keywords:
Conductive
Melt-processable
Eutectic

ABSTRACT

Highly conductive polymers are difficult to process utilizing standard polymer approaches. This report describes a polymer composite loaded with a eutectic metal that is molten during melt processing along with a more traditional Nickel particulate filler. Conductivities over 300 S/cm were achieved, and 60 vol% metals loading was processable with a single screw extruder. The addition of the Nickel particulate was critical for maintaining eutectic dispersion. We anticipate that this approach will facilitate the implementation of conductive polymers into a broader variety of practical applications, due to the enhanced compatibility with standard polymer processing techniques such as extrusion, melt mixing, and resin transfer-molding operations.

1. Introduction

Polymeric materials, which exhibit electrical conductivity approaching pure metals yet retain the flow and formability behavior of standard polymers, have the potential to be utilized in many applications including energy storage devices [1], sensors [2], electronics packaging [3], and EMI shielding [4]. Traditionally, conductivity in polymers is obtained by using either an inherently conductive polymer, or the addition of conductive filler. Inherently conductive polymers, such as polypyrrole and polyaniline typically consist of a rigid and conjugated polymer backbone resulting in high melt viscosities and a melting temperature that can be well above the degradation temperature [5]. This makes most inherently conductive polymers difficult if not impossible to melt process. Alternatively, the addition of conductive fillers such as nickel, silver, or carbon black, typically requires very high loadings to produce conductivity, causing increases in viscosity, poor degassing behavior, and degradation of mechanical performance in some cases. In addition, it can be difficult to disperse particles resulting in inconsistent performance of the material. These issues magnify as the particle size decreases into the sub-micron regime, driven by current trends in device miniaturization. Carbon nanotube based polymer composites are a promising alternative, where conductivity can be achieved at lower filler loadings. However, the conductivity values are typically less than 1 S/cm, and dispersion of the nanotubes with typical polymer processing schemes is difficult [6].

An interesting approach was developed to counter the viscosity rise at high filler loadings by incorporating a eutectic metal to decrease the viscosity of a polymer melt when above the eutectic melting temperature [7]. However, electrical percolation was not observed, resulting in a very low conductivity of $^{\sim}10^{-17}$ S/cm even at 35 vol% eutectic loading [8]. A more recent report demonstrated higher conductivity composites by exploiting small eutectic loadings to enhance particle–particle contacts [9].

In contrast, we report in this paper a melt-processable, highly conductive polymer composite through the addition of a low melting eutectic metal in combination with nickel particulate filler. An important difference in this work is that the eutectic metal represents a majority fraction of the metals loading to improve processability of the composites. In particular, small loadings of solid particulates in the polymer, along with the eutectic, can prevent coalescence of the molten eutectic droplets resulting in intimately dispersed eutectic – particulate – polymer composites that exhibit high conductivity values after melt extrusion. The

---

* Corresponding author. U.S. Army Research Laboratory, Aberdeen, MD 21005, United States. Tel.: +1 410 306 2165; fax: +1 410 306 0676.

** Corresponding author. U.S. Army Research Laboratory, Aberdeen, MD 21005, United States. Tel.: +1 410 306 1940; fax: +1 410 306 0676.

E-mail addresses: randy.mrozek@us.army.mil (R.A. Mrozek), joseph.lenhart1@us.army.mil (J.L. Lenhart).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.04.067

nickel content was held constant at a loading of 10 vol% with increasing eutectic metal loading. Total solids loadings of 60 vol% in a polystyrene matrix were extruded with a single screw extruder. The composite microstructure was observed using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) to map the constituent elements. The images indicate that the eutectic will encapsulate the nickel to provide stability to the dispersed droplets. The resulting composites exhibited uniform extruded cross-sections and no obvious air voids.

2. Experimental

2.1. Materials

Nickel particulate (2–4 μm; Aldrich, Milwaukee, WI) and polystyrene (PS666D, Dow Chemical, Midland, MI) were used as received. The eutectic metal consisting of 58 mass % Bismuth / 42 mass % Tin (Cerro Metal Products, Bellefonte, PA) was received as a 1.5 lb bar. The bar was processed into smaller pieces by melting the metal at 180 °C and pouring the melt through a wire mesh into a water bath. The collected material was dried in a vacuum oven for 18 h at 40 °C.

2.2. Composite processing

Compounding was performed in a Randcastle RCP-0750 single screw extruder (Randcastle Extrusion Systems, Cedar Grove, NJ) at 260 °C. The filler was added in small increments (~2 g filler/10 g polymer material) to avoid screw damage. The extrudate was collected, pelletized, and re-extruded with additional filler. When the desired filler loading was obtained, the composite was re-pelletized and extruded multiple times to ensure uniformity.

2.3. Resistance measurements

The resistance of the extrudate was measured with a Keithley 2410 source meter using a standard 4-wire method. The resistance values were normalized by the sample dimension to obtain the volume resistivity and reported as the volume conductivity (inverse of volume resistivity) in S/cm.

2.4. SEM

SEM images of the composite microstructure were obtained on a Zeiss Supra55VP, field emission gun, scanning electron microscope. The samples were potted in epoxy, polished, coated with a gold-palladium mixture, and imaged with a 5 kV accelerating voltage in high vacuum mode.

3. Results and discussion

The filler system consisted of nickel particulates co-dispersed with a 58% Bismuth/42% Tin eutectic metal. Nickel was utilized due to its electrical conductivity and relative stability to oxidation at room temperature. The eutectic metal has a melting temperature of 138 °C, below the processing temperature of 260 °C but above operational temperature ranges for typical devices. The eutectic was previously explored as a lead-free solder replacement and exhibits good mechanical and electrical connections with nickel [10]. Polystyrene was selected as a model matrix material because it is commercially available in a variety of molecular weights and has well characterized flow behavior to facilitate future investigations regarding the impact of the matrix viscosity and the eutectic-nickel composition on the flow behavior, respectively.

The eutectic metal was added in 10 vol% increments while keeping the nickel content constant at 10 vol% (Table 1). The conductivity values were normalized by the sample dimension and reported as S/cm. The composites exhibited a measurable conductivity at 30 vol% metals loading (10 vol% Ni/20 vol% eutectic) of ~0.1 S/cm (Fig. 1). At 40 vol% metals loading the conductivity increases to 8 S/cm and then begins to plateau at 350 S/cm at 60 vol % metals loading. In addition, the composites maintain the conductivities over large length scales. For example, a 65 cm strand of extrudate with a 3 mm diameter exhibited an end-to-end resistance < 1.3 Ω. Control samples containing 20 vol% nickel particulate without eutectic exhibited reasonable conductivity values of 0.1 S/cm. When the loading was increased to 30 vol% nickel particulate, the conductivity increased to 10 S/cm however, the material was an unprocessable paste with large void content. The 30 vol% nickel loading resulted in congestion in the extrusion nozzle and failure of the extruder burst disc during processing.

Table 1
Composition of individual sample constituents.

Total metal content (vol%)	Nickel (vol%)	Eutectic (vol%)	Polystyrene (vol%)
30	10	20	70
40	10	30	60
50	10	40	50
60	10	50	40

The incorporation of nickel particulate is critical to dispersing large quantities of eutectic metal. In the absence of the nickel particulate, the eutectic would coalesce into large droplets with loadings larger than a few volume percent, resulting in a non-conductive composite structure. With 10 vol% nickel particulates, the eutectic was well dispersed in the polystyrene matrix, and the composite exhibited substantial conductivity. Several potential explanations can describe the nickel facilitated dispersion of liquid eutectic including: the nickel acts as a mechanical aid during mixing; the nickel modifies the viscosity of the eutectic droplets and slows the coalescence process similar to the dispersed phase in an immiscible polymer blend [11]; the particulates act as wetting sites for the liquid eutectic forcing eutectic dispersion as the nickel particulates become increasingly dispersed; or some combination of these mechanisms. While the mechanism for the nickel facilitated dispersion is unclear, control experiments illustrated the

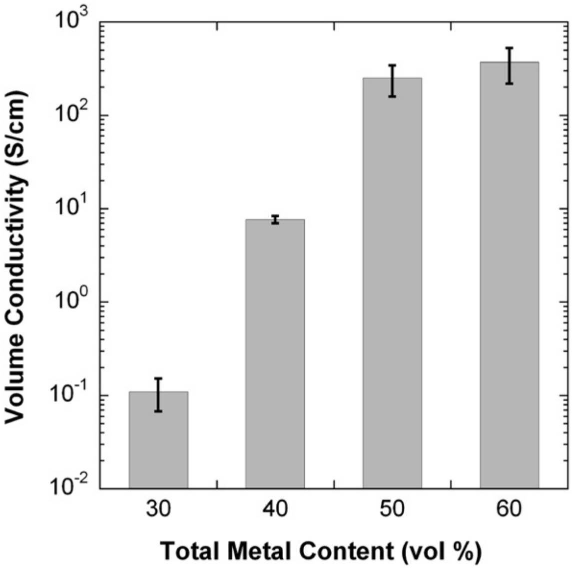


Fig. 1. Sheet conductivity at different total metal contents with a constant nickel particulate loading of 10 vol%.

importance of the nickel surface chemistry and eutectic – nickel wettability. If the nickel particulates were heated to generate an oxide coating, the oxide-coated nickel did not facilitate eutectic dispersion, and eutectic loadings of only a few volume percent were possible. SEM images of the composites provided additional insight. At low filler loadings (10 vol% Ni/10 vol% eutectic, Fig. 2a), the filler dispersion consisted of nickel particulates in the polystyrene matrix and isolated larger islands of eutectic metal that

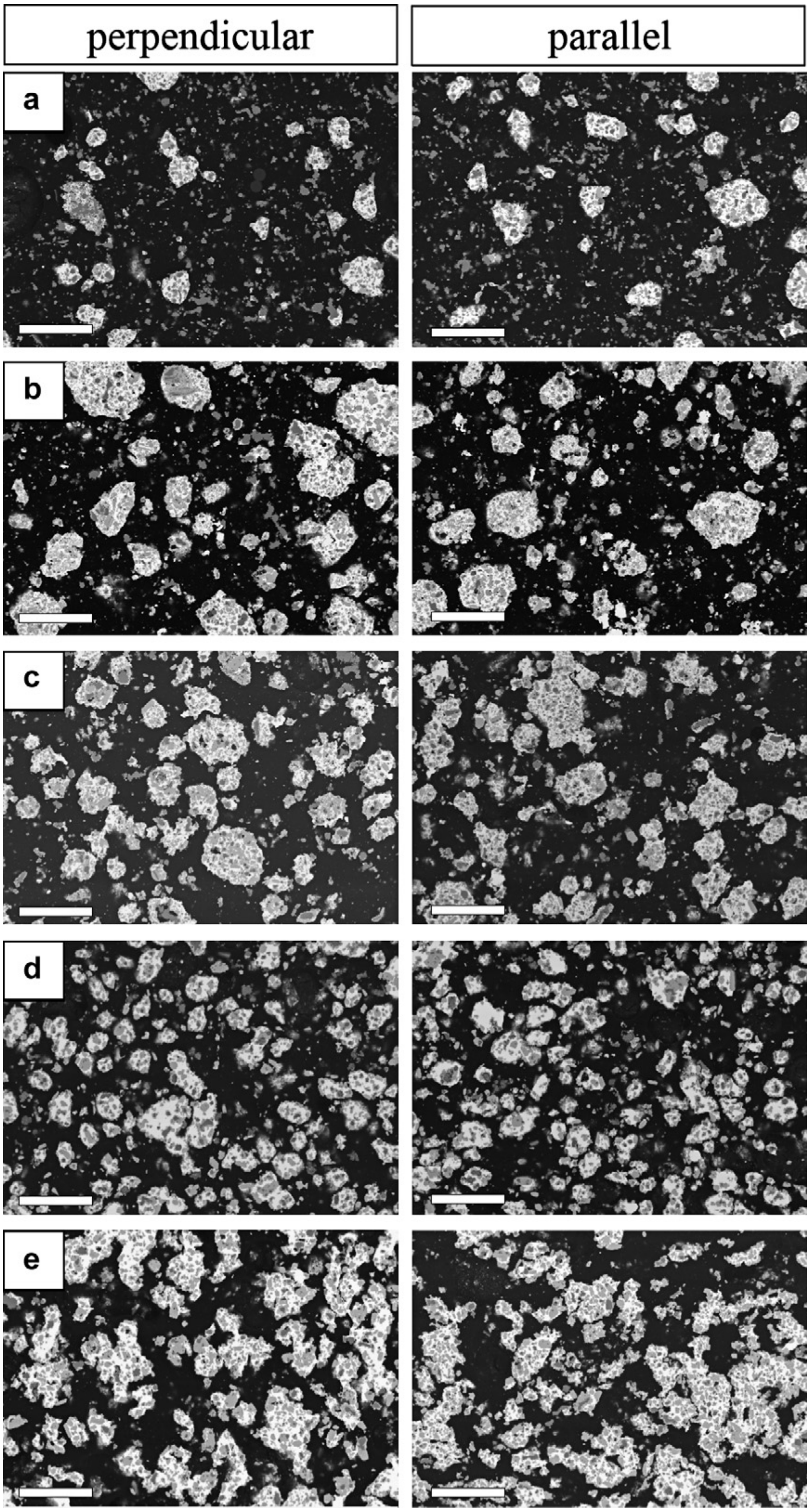


Fig. 2. SEM images of composite samples containing 10 vol% nickel along with a) 10, b) 20, c) 30, d) 40, and e) 50 vol% eutectic in a polystyrene matrix cross-sectioned perpendicular (LEFT) and parallel (RIGHT) to the extrusion direction. Scale bars are 50 um long. Black is polystyrene, light gray is Ni particulate, and white is eutectic.

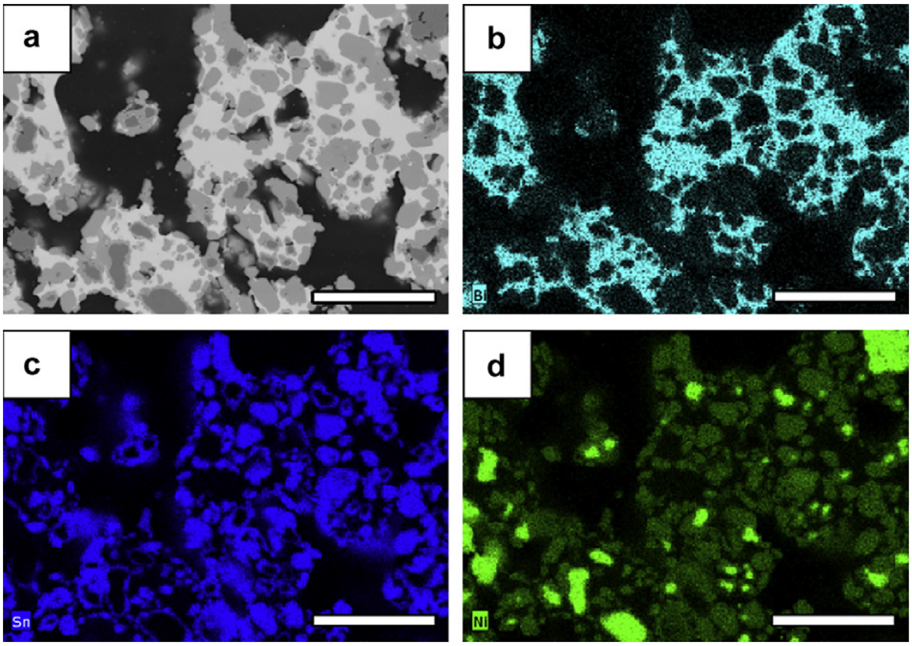


Fig. 3. a) SEM image of polystyrene containing 10 vol% nickel/50 vol% eutectic where black is polystyrene, light gray is Ni particulate, and white is eutectic. EDX maps of b) bismuth, c) tin, and d) nickel. Scale bars are 50 um long.

encapsulate the remaining particles. As the eutectic loading increases to 20 vol% and 30 vol%, Fig. 2b and c respectively, the nickel particulates were increasingly engulfed by the eutectic. The composite microstructure evolved to islands of a eutectic/Ni composite dispersed in the polymer matrix. While in the cross-sectional SEM images it is not obvious, the islands were not completely isolated, since the conductivity of 8 S/cm with the 10 vol % Ni/30 vol% eutectic formulation is consistent with a reasonably percolated structure. With 40 vol% and 50 vol% eutectic the Ni particulates are completely encapsulated by the eutectic and the Ni/eutectic “islands” exhibit substantial connectivity even in the SEM images, which provides the higher electrical conductivity for these samples. The gradual encapsulation of nickel with eutectic, coupled with the observation that oxidized nickel particulates did not facilitate eutectic dispersion, demonstrates that the eutectic wettability of the solid filler and the resulting filler-eutectic interfacial region that forms during processing is a critical factor for preventing coalescence of the liquid metal. Exploration of this eutectic as a lead-free solder replacement showed that a Ni_3Sn_4 interfacial alloy formed in the range of 180–300 °C, consistent with the processing temperature of these composites [10]. Cross-sectional images obtained both parallel and perpendicular to the extrusion direction did not exhibit any noticeable anisotropy (Fig. 2).

To gain additional insight into the co-operative interaction of the nickel particulate and eutectic metal, the constituent elements were mapped in the SEM using energy dispersive x-ray spectroscopy (EDX). Fig. 3 contains an SEM image of a 60 vol% metal loading sample along with elemental maps obtained from EDX for bismuth, tin, and nickel. These images verify a high concentration of nickel with the eutectic, while outside the eutectic little nickel is observed. Inside the metal rich regions, the nickel and tin signals largely overlap and are surrounded by the bismuth. This indicates that during the eutectic encapsulation of nickel, the eutectic phase separates, typical of eutectics, and the nickel nucleates the tin. Whether this indicates that the tin has some affinity for the nickel or the nickel simply provides a solid surface to facilitate nucleation is unclear. As mentioned previously this eutectic was examined as a lead-free solder for use with nickel electrodes and formed a thin continuous layer of Ni_3Sn_4 interfacial alloy in the range of 180–300 °C [10].

4. Conclusions

This report describes a melt-processable polymer composite that exhibits high electrical conductivity based on a low melting eutectic metal and a traditional nickel particulate filler. Through this approach, metal loadings of 60 vol% were produced while maintaining the ability to melt process the composite. The incorporation of 10 vol% nickel was vital for obtaining high eutectic loadings, and maintaining eutectic dispersion. The surface chemistry of the Ni filler was important as eutectic – filler wettability were critical for preventing eutectic coalescence. While we hypothesize that the generality of this approach can be expanded to other composite systems, it will certainly have some limitations within the confines of processing windows, filler-polymer-eutectic interactions, and viscosity ratios which, at this time, we have not fully investigated. Ongoing research is focused on outlining those details by examining the impact of Ni loading and processing conditions on the resulting composite morphology, as well as the incorporation of other filler types such as Ni nanoparticulates, Ni coated graphite fibers, carbon nanotubes and carbon nanofibers, and even silica particulates with various surface chemistries. In addition, we are investigating the generality of this approach in other polymer matrices. We anticipate that this work will lead to implementation of conductive polymers into a variety of applications using traditional melt processing techniques.

Acknowledgements

This work was initiated at Sandia National Laboratories by J.L. Lenhart, P.J. Cole, and R.A. Mrozek and is being continued at the US Army Research Laboratory by J.L. Lenhart and R.A. Mrozek. R.A. Mrozek was funded at ARL through a contract with the Oak Ridge Institute of Science and Engineering (ORISE). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of

Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedures and does not imply recommendations by the Army Research Laboratory.

References

[1] Khomenko V, Frackowiak E, Beguin F. Electrochim Acta 2005;50:2499–506.
[2] Gerard M, Chaubey A, Malhorta BD. Biosens Bioelectron 2002;17:345–59.
[3] Sun M. Microelectron. J. 2001;32:197–203.
[4] Chung DDL. Carbon 2001;39:279–85.
[5] Wessling B. Synth Met 1998;143–154.
[6] (a) Ramasubramaniam R, Chen J, Liu H. Appl Phys Lett 2003;83:2928–30;
(b) Du F, Scogna RC, Zhou W, Brand S, Fischer JE, Winey KI. Macromolecules 2004;37:9048–55;
(c) Isayev AI, Kumar R, Lewis TM. Polymer 2009;50:250–60;
(d) Haggenmueller R, Du F, Fischer JE, Winey KI. Polymer 2006;47:2381–8.
[7] Zhang X, Pan Y, Cheng J, Yi XJ. Mater Sci 2000;35:4573–81.
[8] (a) Zhang X, Pan Y, Shen L, Yi XJ. Appl Polym Sci 2000;77:756–63;
(b) Zhang X, Pan Y, Shen L, Zheng Q, Yi XJ. Appl Polym Sci 2000;77:1044–50.
[9] Michaeli W, Pfefferkorn TG. Polym Eng Sci 2009;49:1511–24.
[10] Tao WH, Chen C, Ho CE, Chen WT, Kao CR. Chem Mater 2001;13:1051–6.
[11] Yang H, Shibayama M, Stein RS, Shimizu N, Hashimoto T. Macromolecules 1986;19:1667–74.